Supporting Information

(4-Ferrocenylphenyl)propargyl ether derived carbohydrate triazoles: Influence of a hydrophobic linker on the electrochemical and cytotoxic properties

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General procedure for the synthesis of carbohydrate azides (2c and 2e)

To a stirred solution of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (1.1 equiv.) in anhydrous dichloromethane, a solution of acid chloride (1 equiv.) and triethylamine was added drop wise. The reaction mixture was stirred for 6 h at room temperature and then quenched with water. The reaction mixture was extracted with dichloromethane, washed with water and dried in vacuum. The resulting crude product was purified by column chromatography.

3-*O*-Acetyl-5-azido-5-deoxy-1,2-*O*-isopropylidene-*α*-D-xylofuranose (2c)

The reaction of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**2b**) (473 mg, 2.2 mmol) with acetyl chloride (156 mg, 2 mmol) resulted **2c** as colourless liquid. Yield: 0.46 g (89%); $[\alpha]_D^{24}$ -16.18 (c 1.8, $CHCl_3$); IR (neat, ν_{max}, cm^{-1}): 2988, 2103, 1749, 1376, 1222, 1071; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.13 (s, 3H, C*H*$_3$), 1.52 (s, 3H, C*H*$_3$), 2.11 (s, 3H, C*H*$_3$), 3.41-3.54 (m, 2H, H-5), 4.38-4.43 (m, 1H, H-4), 4.54 (d, 1H, ***J*** = 3.7 Hz, H-2), 5.20 (d, 1H, ***J*** = 2.8 Hz, H-3), 5.93 (d, 1H, ***J*** = 3.7 Hz, H-1); ^{13}C (75.5 MHz, $CDCl_3$): δ (ppm) = 20.63, 26.14, 26.62, 49.13, 76.23, 77.52, 83.35, 104.71, 112.29, 169.60; ESI (in CH_3OH): *m/z* 258 $[M+H]^+$; Anal. calc. for $C_{10}H_{15}N_3O_5$ (257.24): C 46.69, H 5.88, N 16.33; found: C 46.42, H 5.72, N 16.18.

5-Azido-3-benzoyl-5-deoxy-1,2-*O*-isopropylidene-*α*-D-xylofuranose (2e)

The reaction of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**2b**) (473 mg, 2.2 mmol) with benzoyl chloride (280 mg, 2 mmol) resulted **2e** as colourless liquid. Yield: 0.58 g (91 %); $[\alpha]_D^{25}$ -1.78 (c 1.8, $CHCl_3$); IR (neat, ν_{max}, cm^{-1}): 3069, 2990, 2103, 1788, 1725, 1266,1067; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.35 (s, 3H, C*H*$_3$), 1.58 (s, 3H, C*H*$_3$), 3.53-3.54 (m, 1H, H-5), 3.60-3.64 (m, 1H, H-5), 4.53-4.65 (m, 1H, H-4), 4.69 (d, 1H, ***J*** = 2.9 Hz,

H-2), 4.58 (d, 1H, ***J*** = 2.0 Hz, H-3), 6.03 (d, 1H, ***J*** = 2.9 Hz, H-1), 7.48 (t, 2H, ***J*** = 7.9 Hz, Ar), 7. 62 (t, 1H, ***J*** = 7.9 Hz, Ar), 8.04 (d, 2H, ***J*** = 7.9 Hz, Ar); ^{13}C (75.5 MHz, $CDCl_3$): δ (ppm) 26.13, 26.62, 49.29, 76.57, 77.84, 83.38, 104.80, 112.36, 128.54, 128.88, 129.65, 133.64, 165.10; ESI-MS (in CH_3OH): *m/z* 320 $[M+H]^+$; Anal. calc. for $C_{15}H_{17}N_3O_5$ (319.31): C 56.42, H 5.37, N 13.16; found: C 561.26, H 5.10, N 12.94.

Figure S1: ^{1}H NMR spectrum of **1**

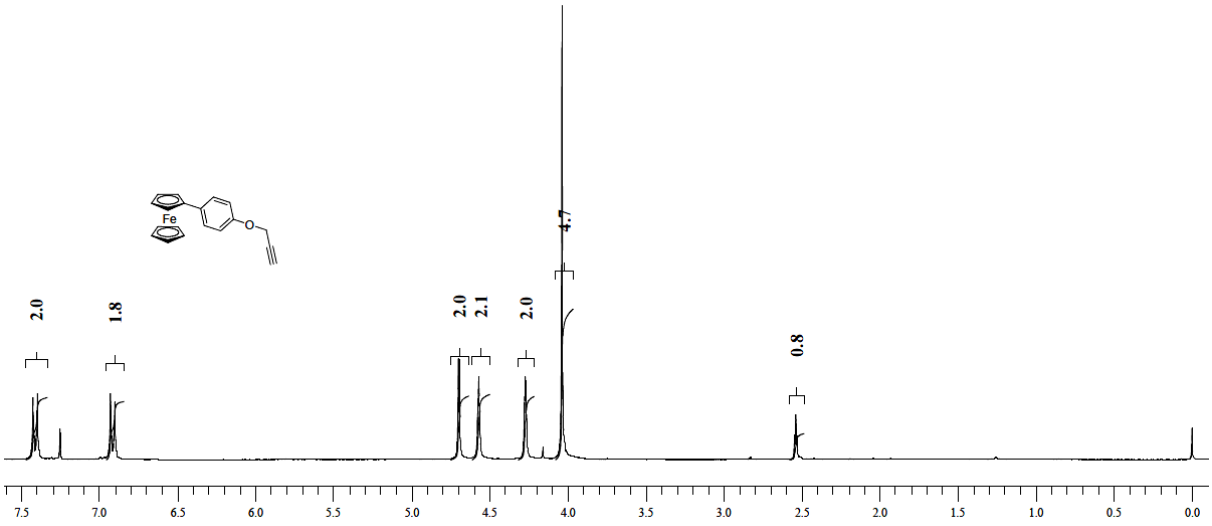


Figure S2: ^{13}C NMR spectrum of **1**

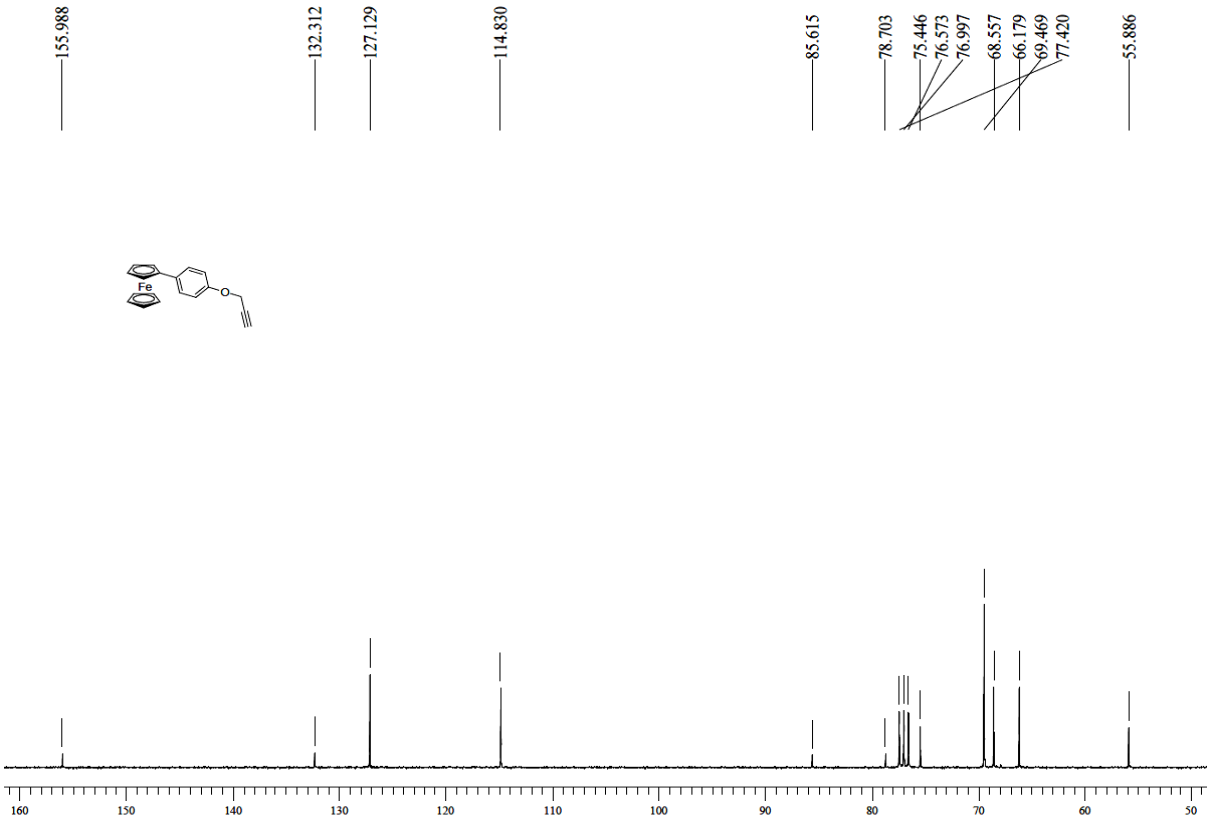


Figure S3: ^{1}H NMR spectrum of **3a**

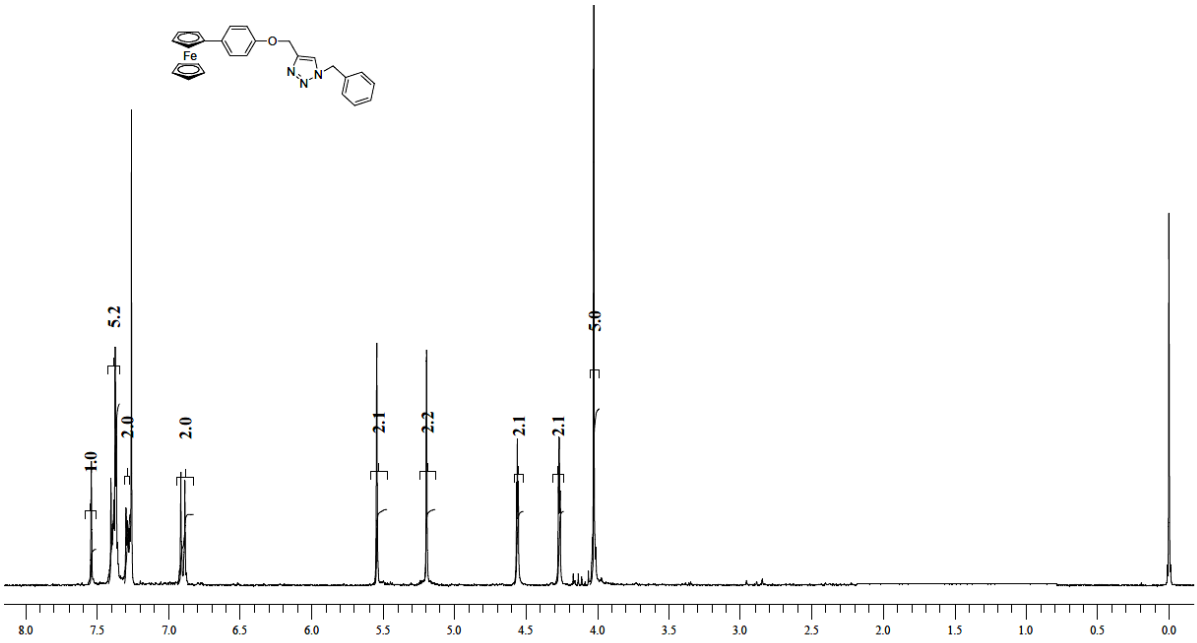


Figure S4: ^{13}C NMR spectrum of **3a**

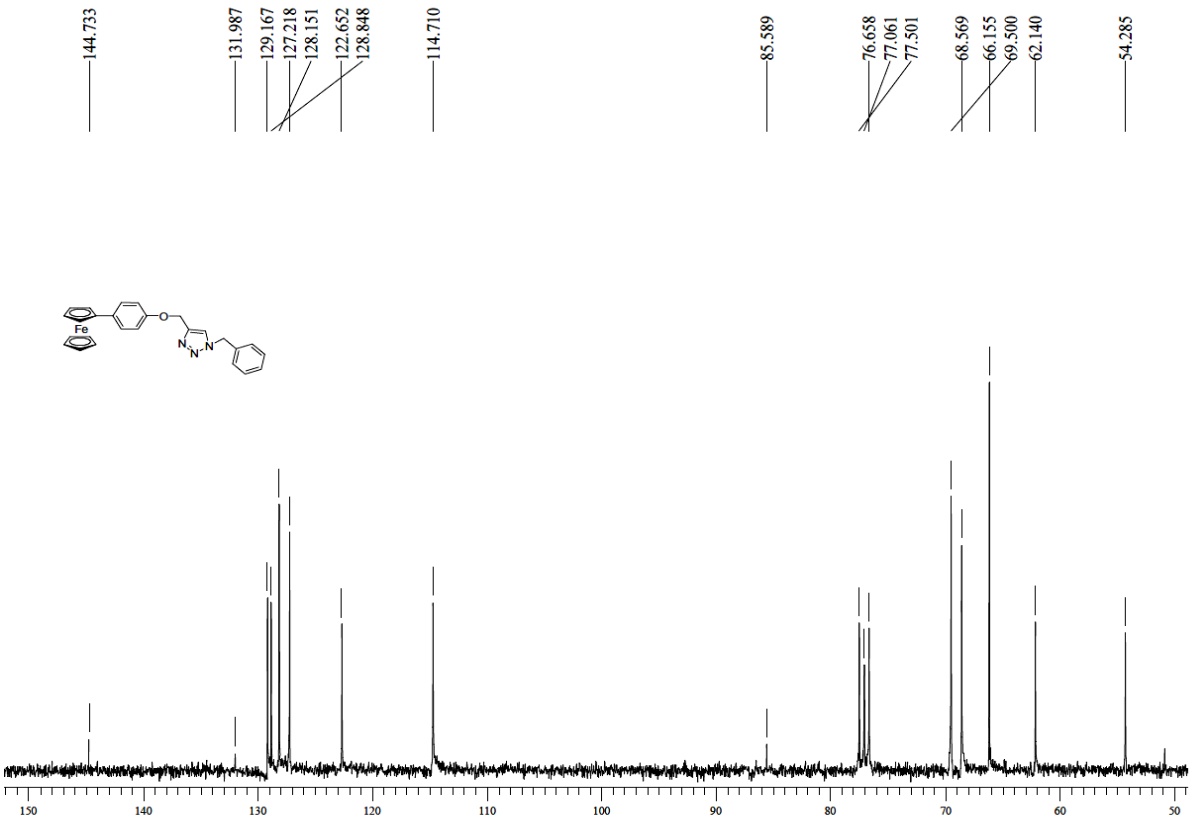


Figure S5: ^{1}H NMR spectrum of **3b**

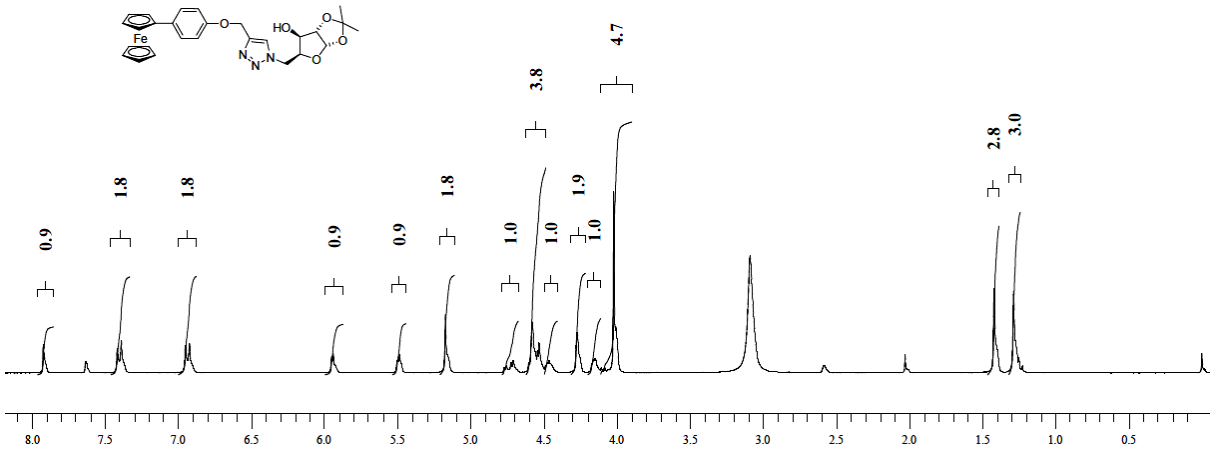


Figure S6: ^{13}C NMR spectrum of **3b**

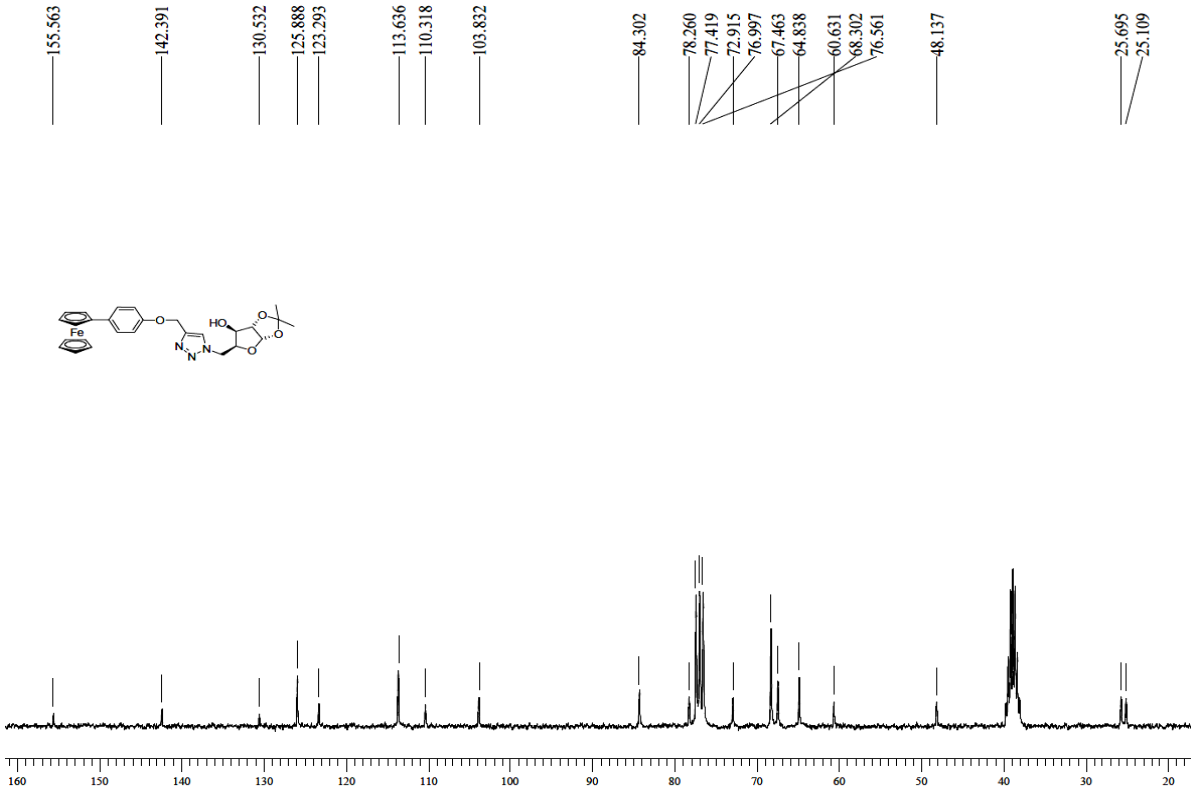


Figure S7: ^{1}H NMR spectrum of **3c**

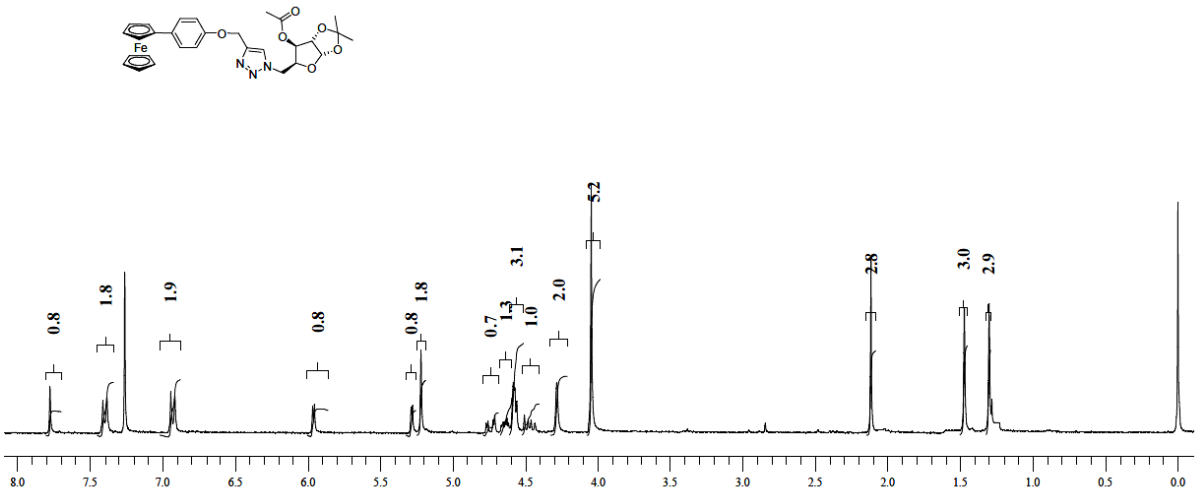


Figure S8: ^{13}C NMR spectrum of **3c**

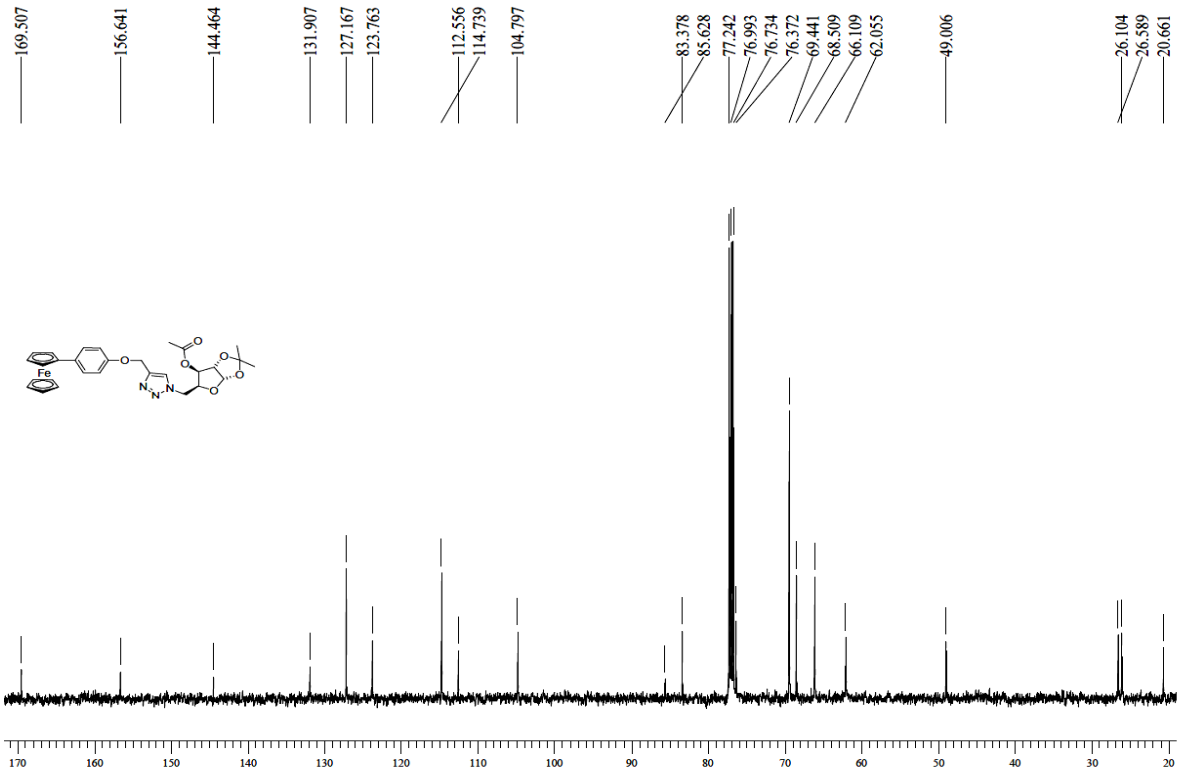


Figure S9: ^{1}H NMR spectrum of **3d**

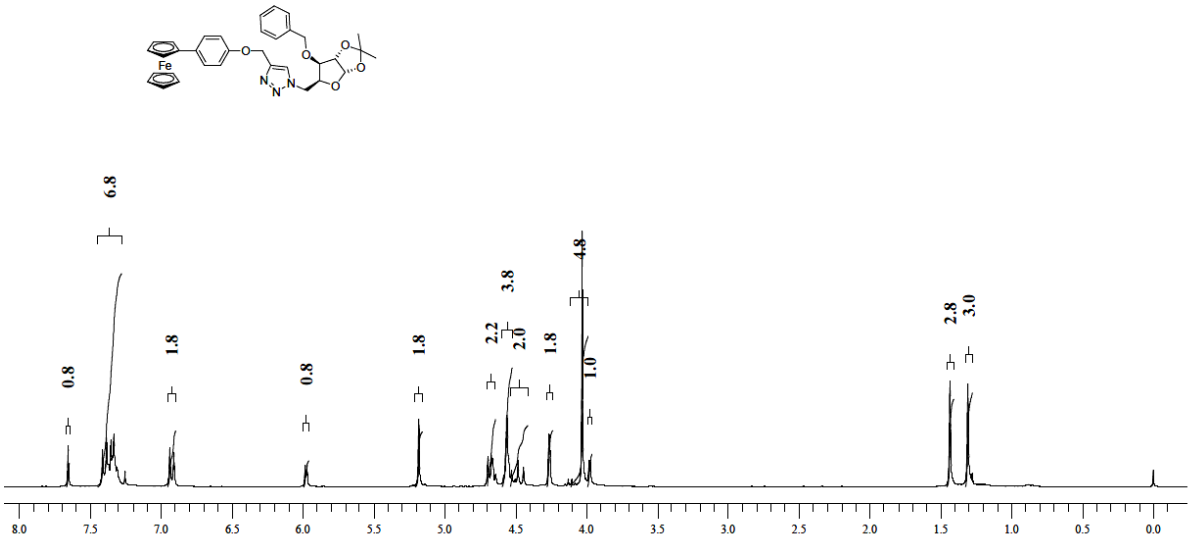


Figure S10: ^{13}C NMR spectrum of **3d**

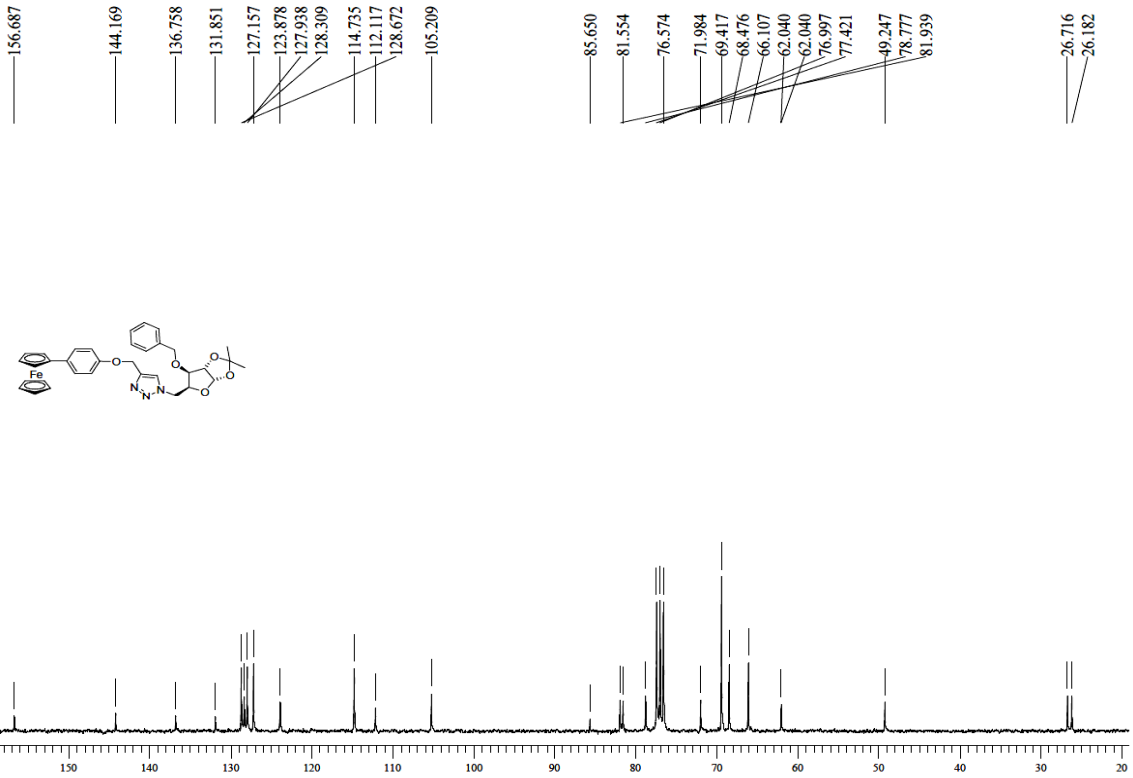


Figure S11: ^{1}H NMR spectrum of **3e**

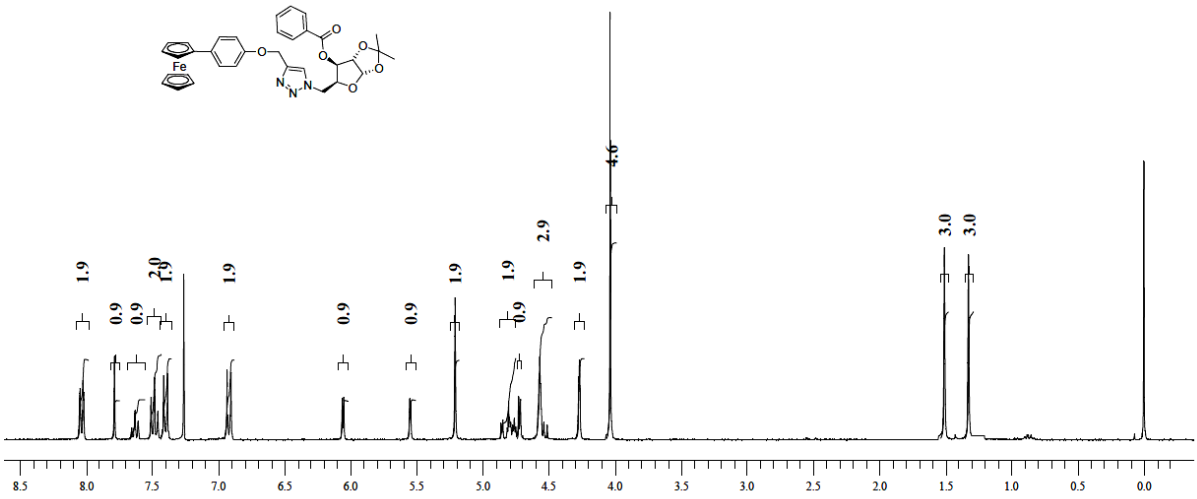


Figure S12: ^{13}C NMR spectrum of **3e**

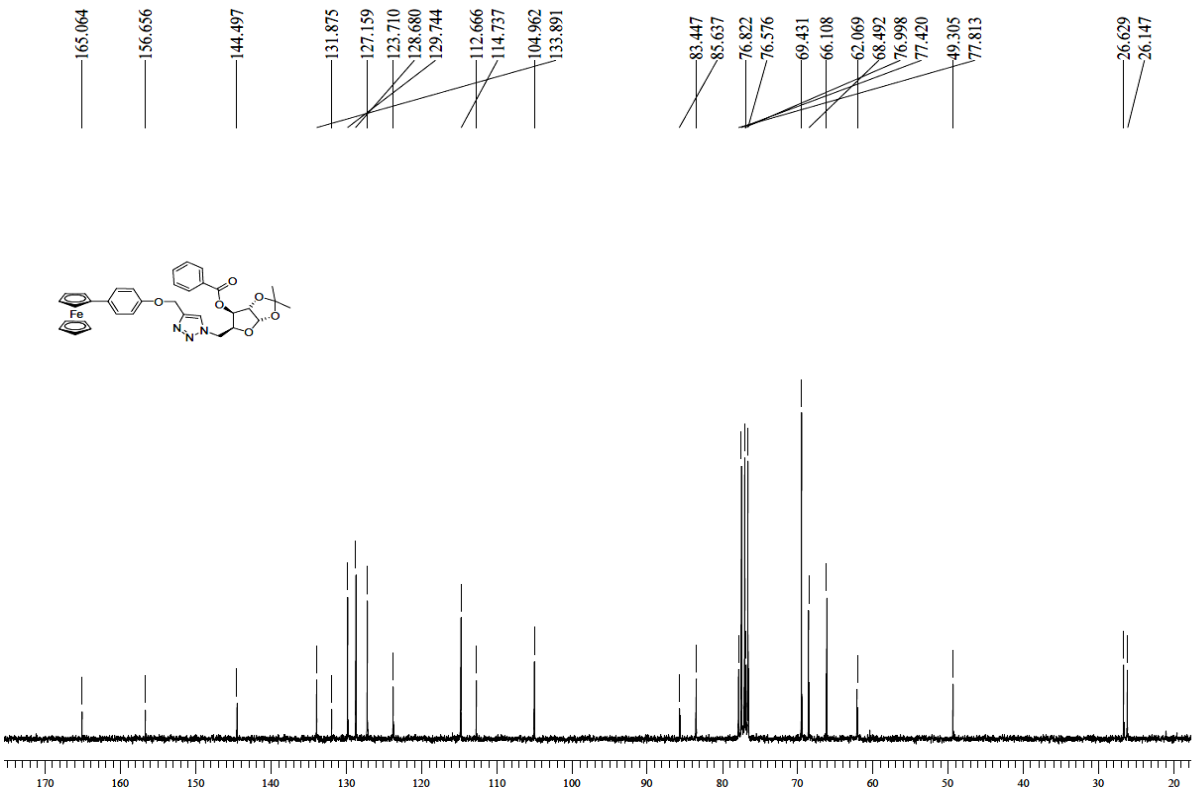


Figure S13: ^{1}H NMR spectrum of **3f**

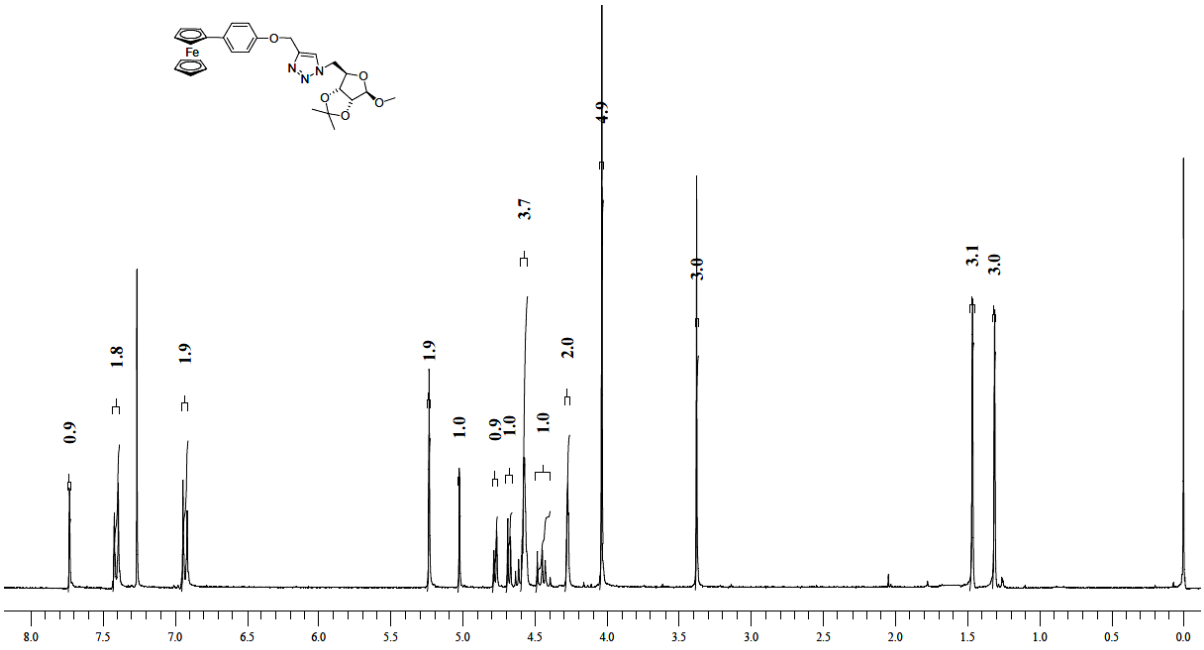


Figure S14: ^{13}C NMR spectrum of **3f**

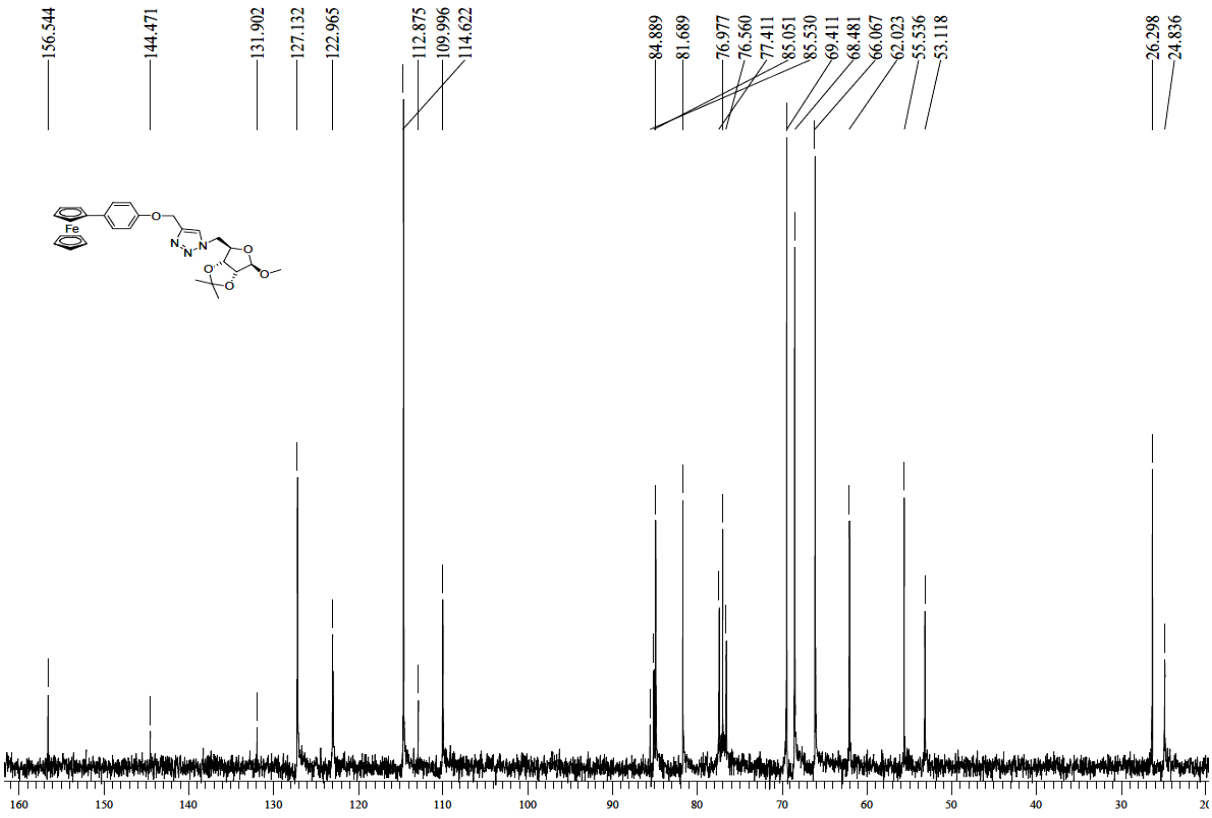


Figure S15: ^{1}H NMR spectrum of **3g**

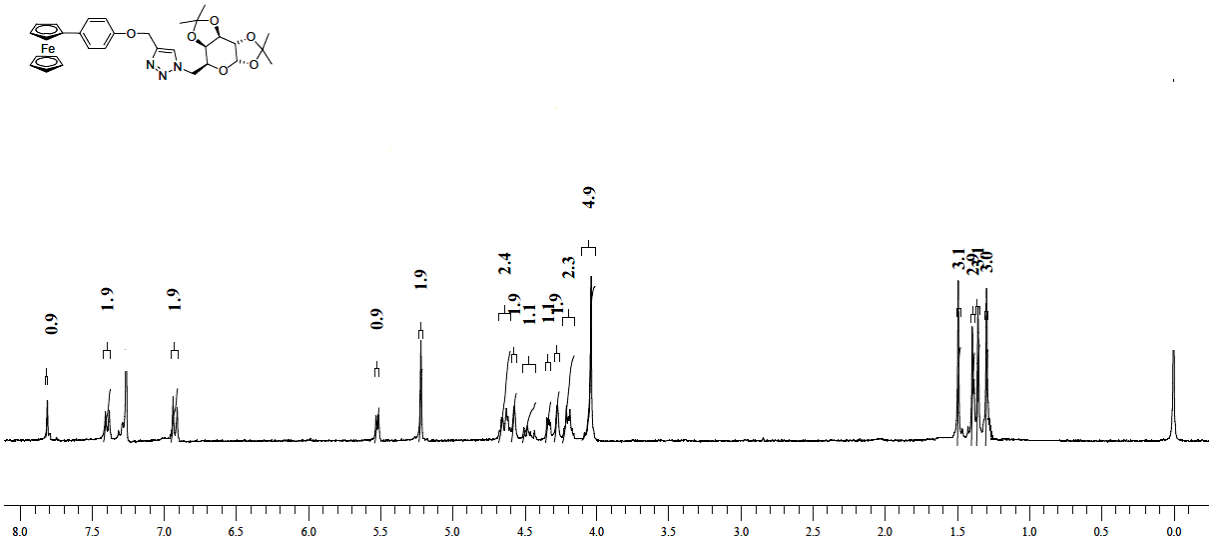


Figure S16: ^{13}C NMR spectrym of **3g**

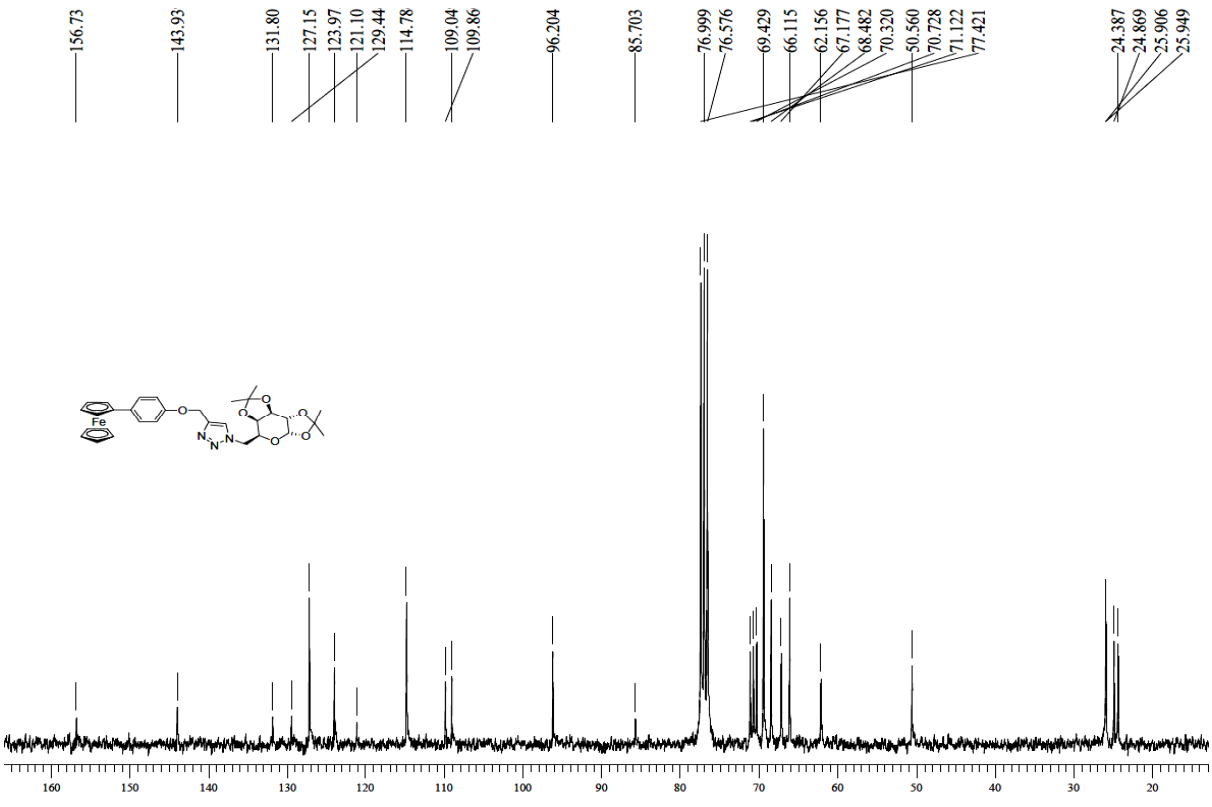


Figure S17: ^{1}H NMR spectrum of **3h**

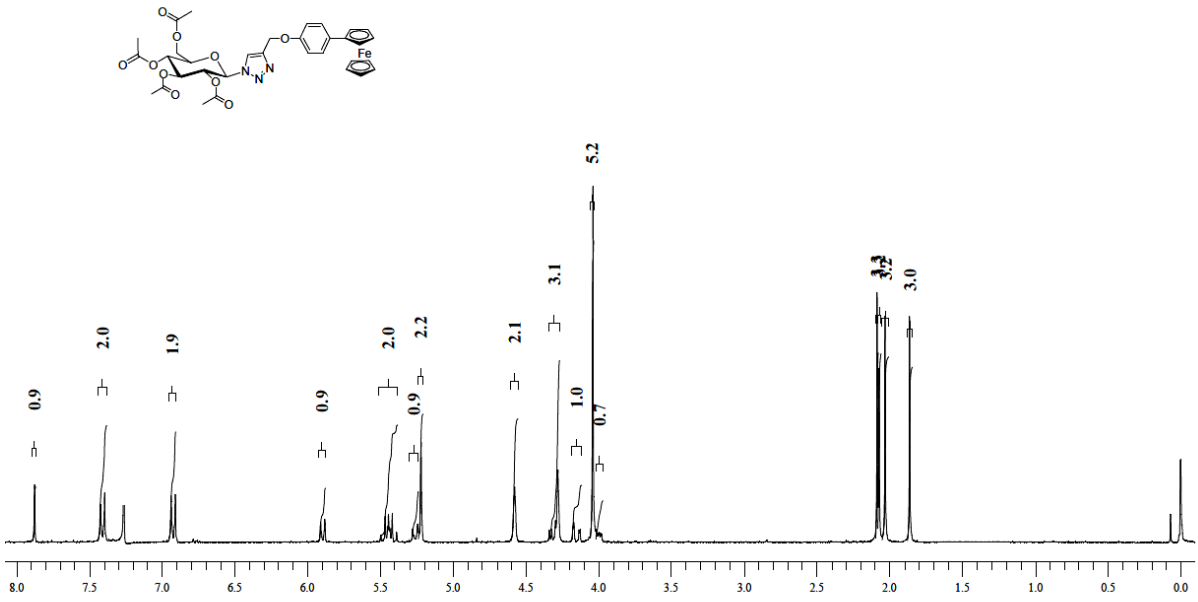
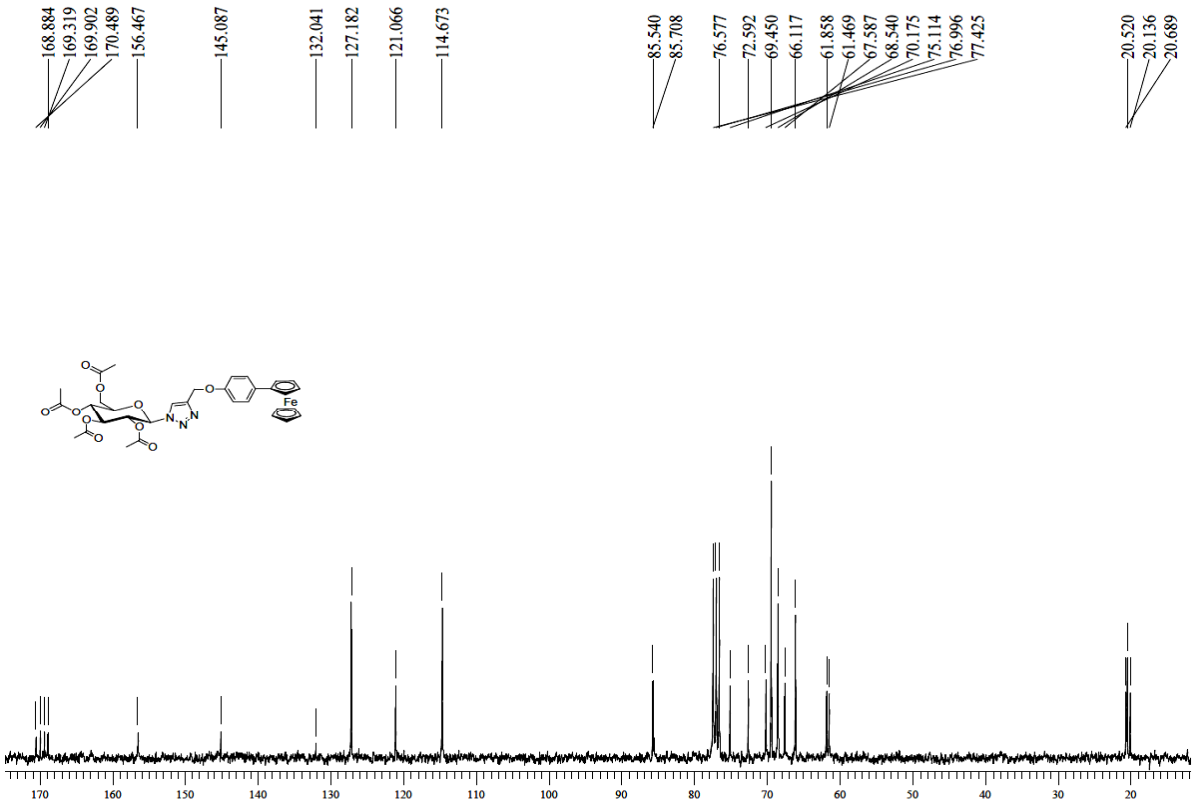


Figure S18: ^{13}C NMR spectrum of **3h**



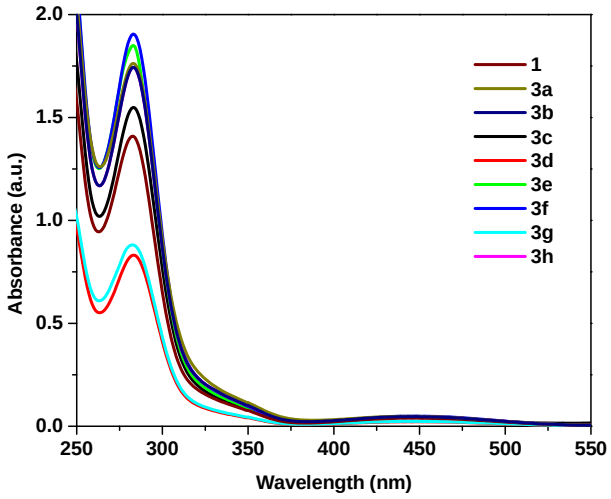


Figure S19: UV-Visible spectra of alkyne (**1**) and ferrocene conjugates **3a-h** in 0.1mM dichloromethane solution

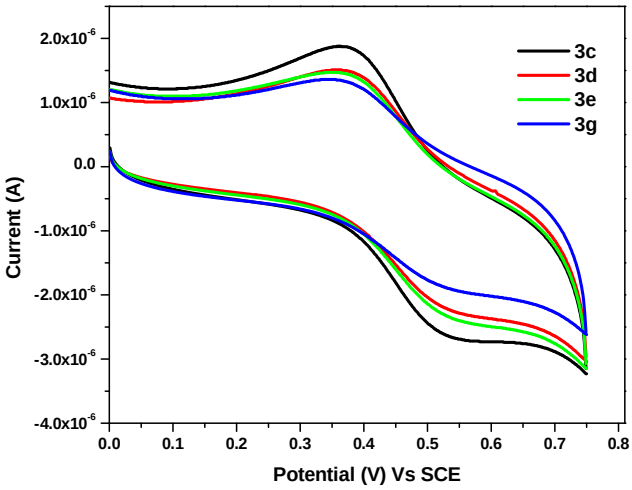


Figure 20: Cyclic voltammograms of ferrocene carbohydrate conjugates **3c**, **3d**, **3e** and **3g** in dichloromethane solution.

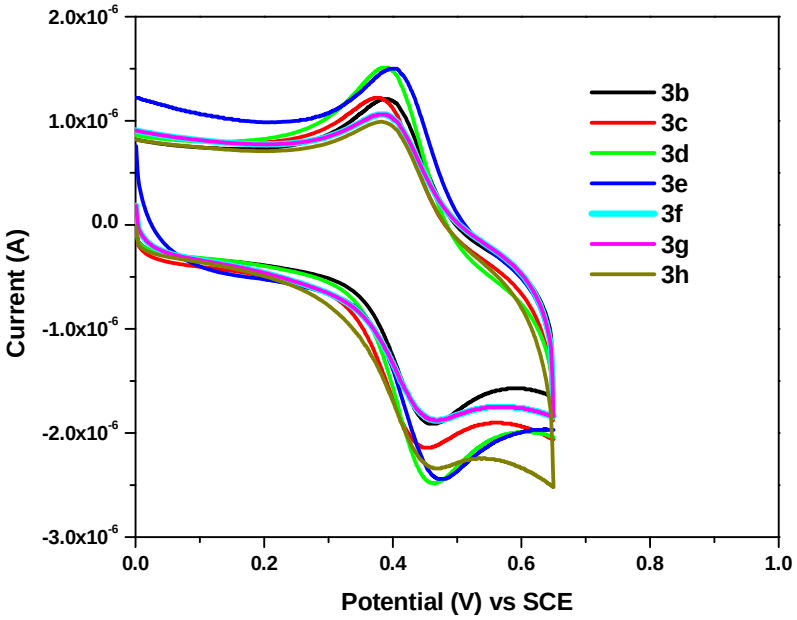


Figure S21: Cyclic voltammograms of ferrocene carbohydrate conjugates in 0.2 mM DMSO solution.

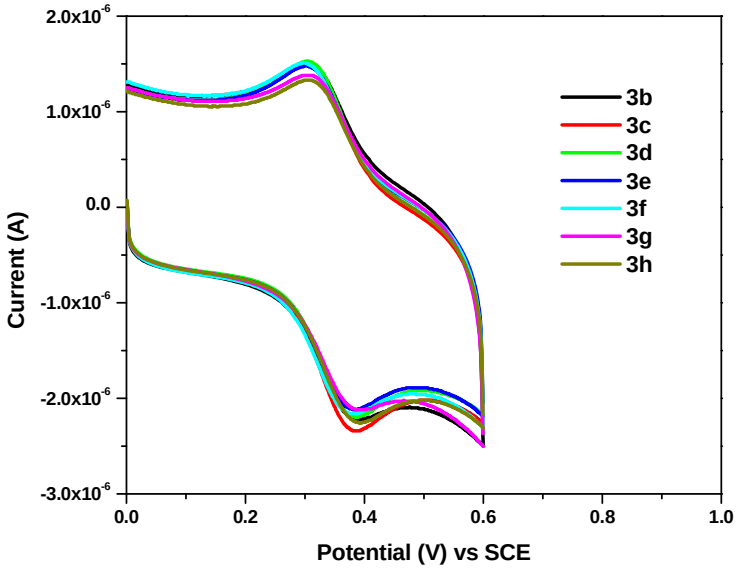


Figure S22: Cyclic voltammograms of ferrocene-carbohydrate conjugates in DMSO and phosphate buffer solution (pH 7.4).

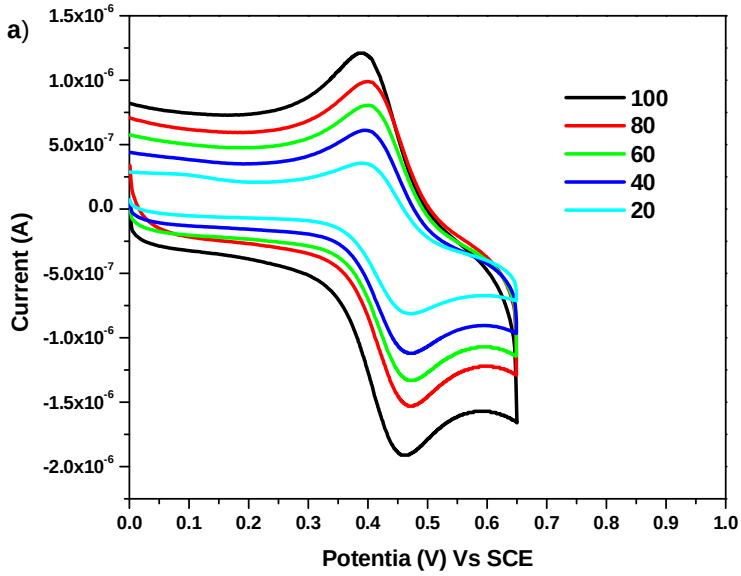


Figure S23: Cyclic voltammograms of **3b** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

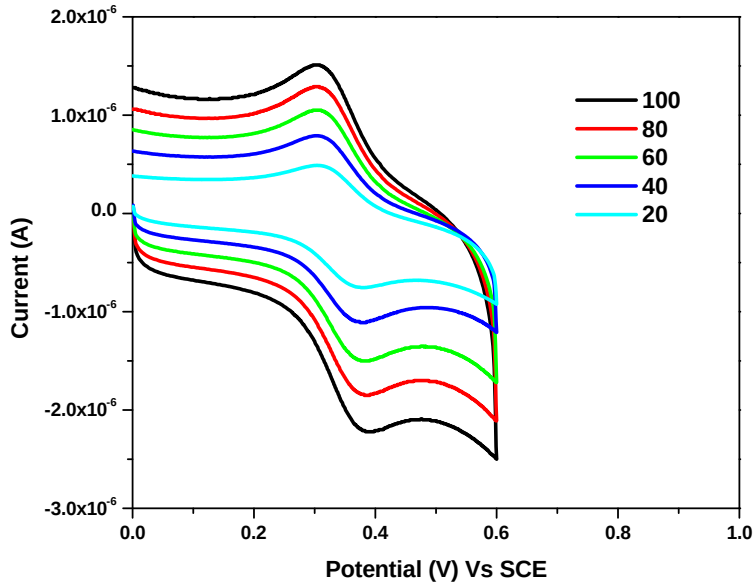


Figure S24: Cyclic voltammograms of **3b** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

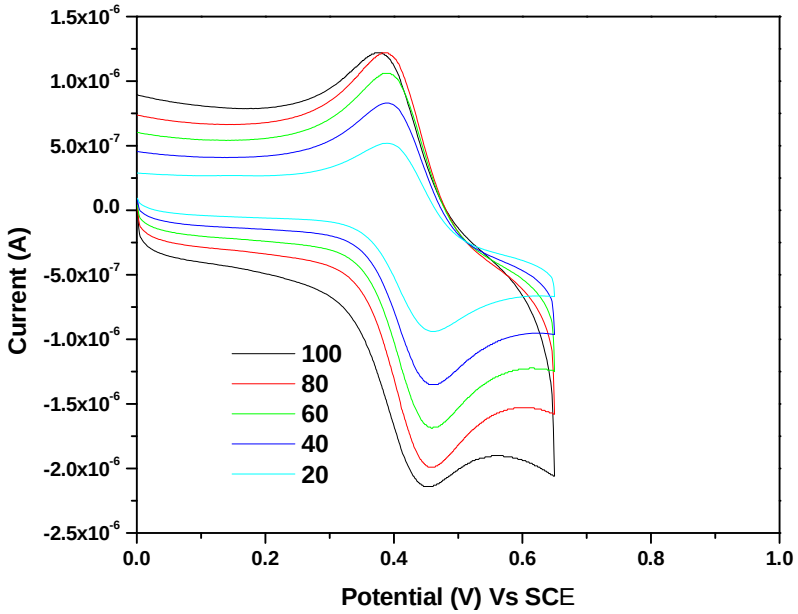


Figure S25: Cyclic voltammograms of **3c** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

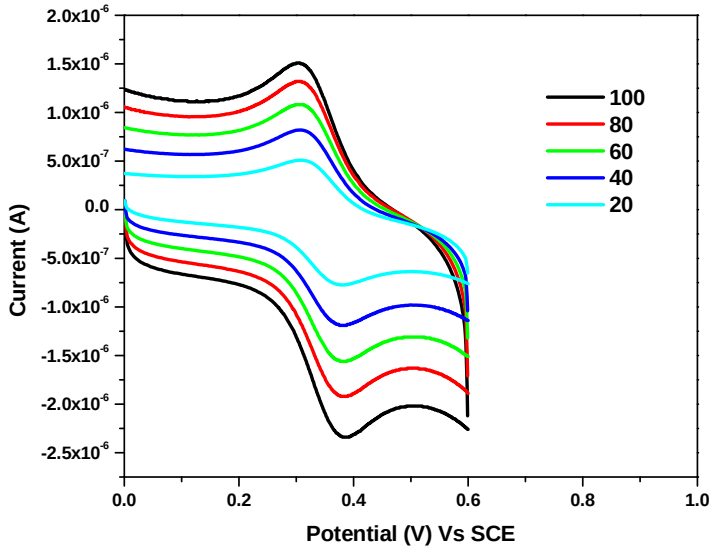


Figure S26: Cyclic voltammograms of **3c** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

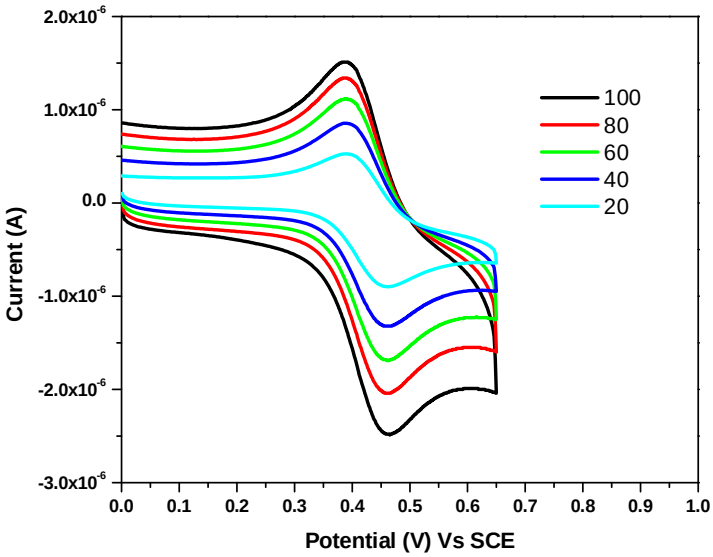


Figure S27: Cyclic voltammograms of **3d** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

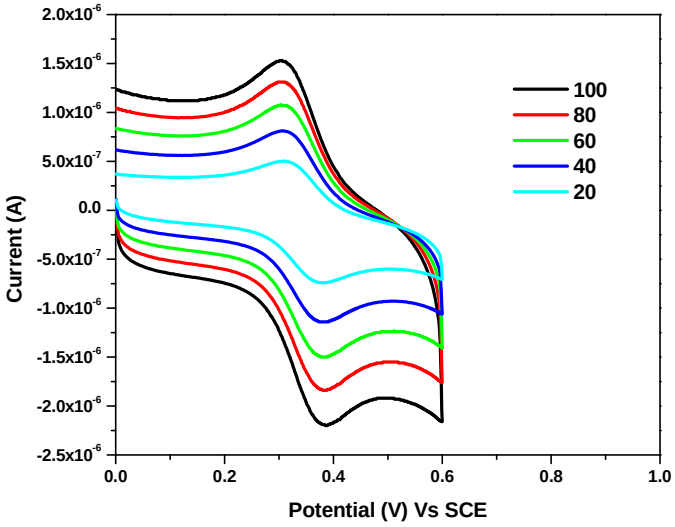


Figure S28: Cyclic voltammograms of **3d** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

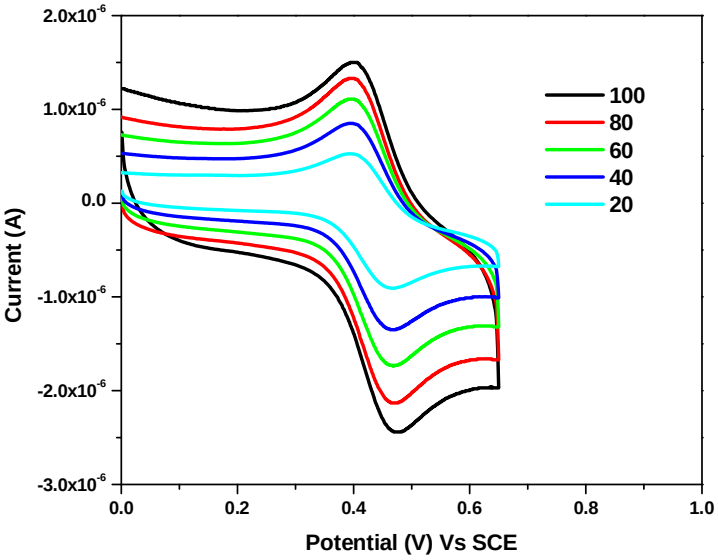


Figure S29: Cyclic voltammograms of **3e** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

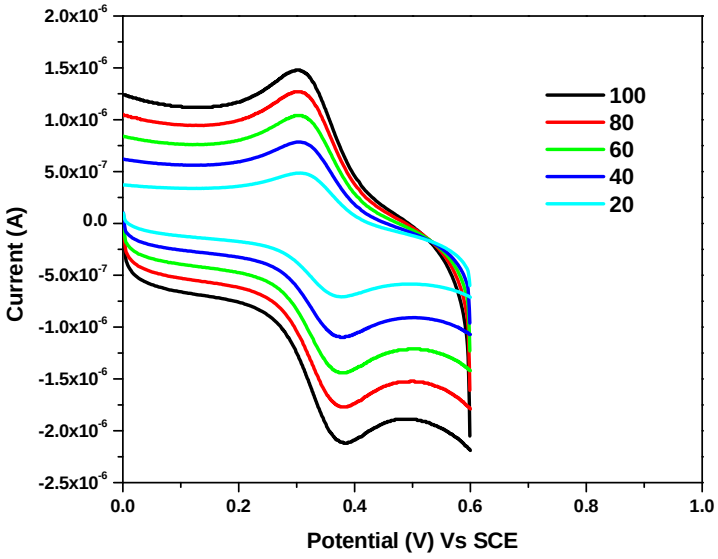


Figure S30: Cyclic voltammograms of **3e** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

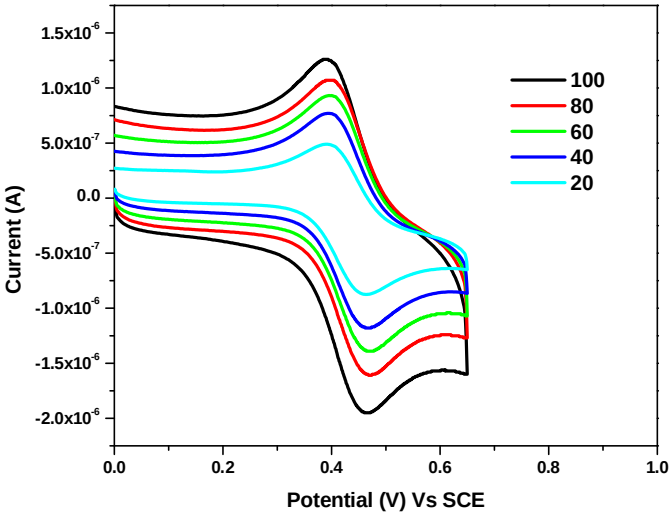


Figure S31: Cyclic voltammograms of **3f** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

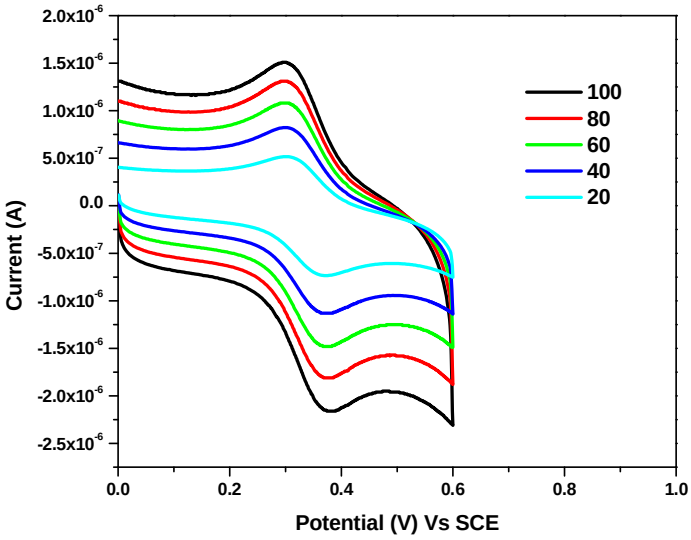


Figure S32: Cyclic voltammograms of **3f** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

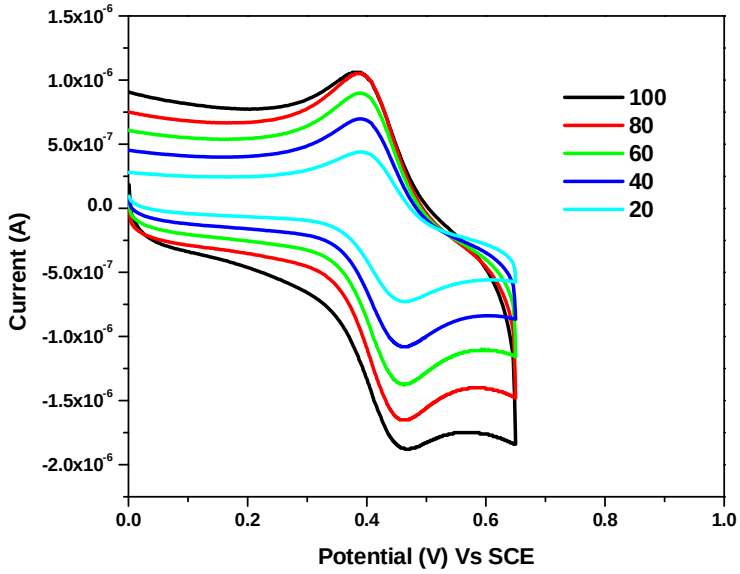


Figure S33: Cyclic voltammograms of **3g** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

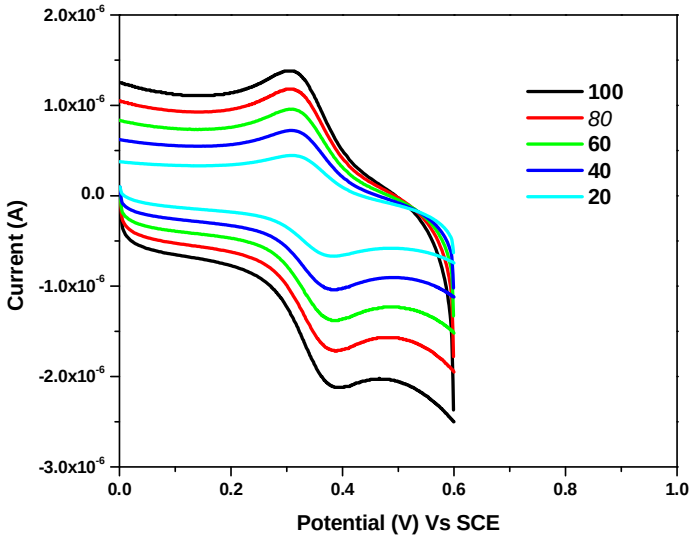


Figure S34: Cyclic voltammograms of **3g** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

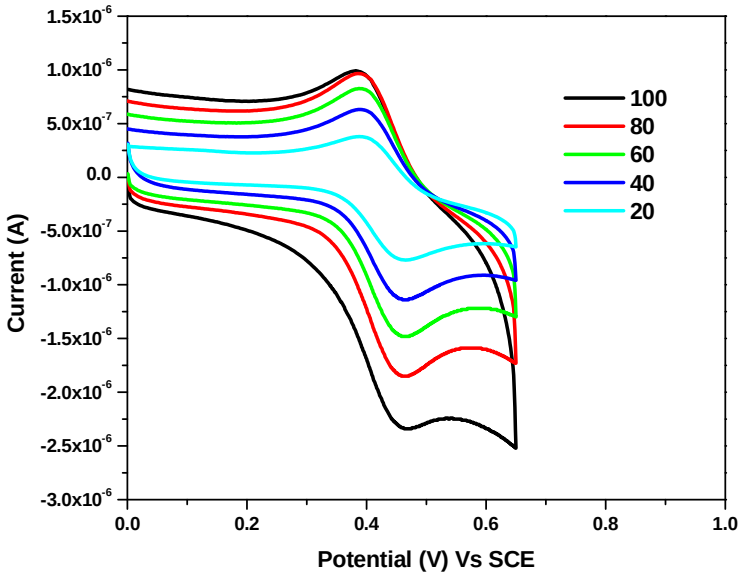


Figure S35: Cyclic voltammograms of **3h** in 0.2 mM DMSO solution at different scan rates at 25 ^{o}C

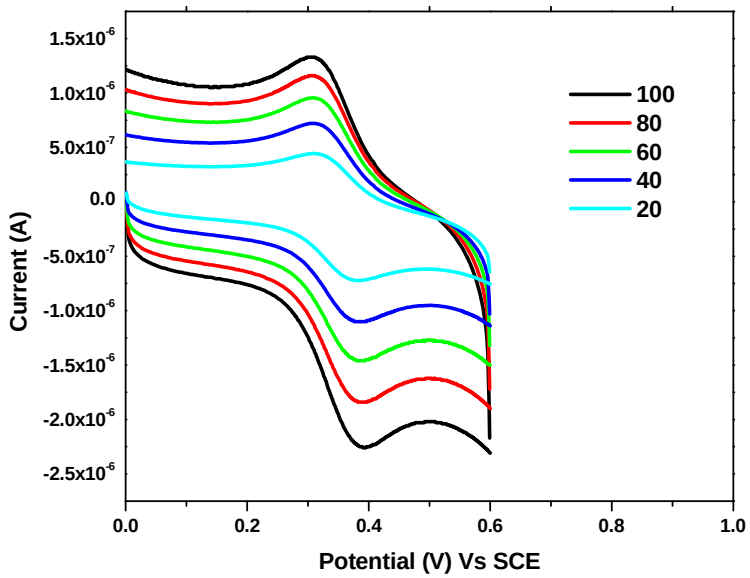


Figure S36: Cyclic voltammograms of **3g** in DMSO and phosphate buffer (2:1) solution at different scan rates at 25 ^{o}C

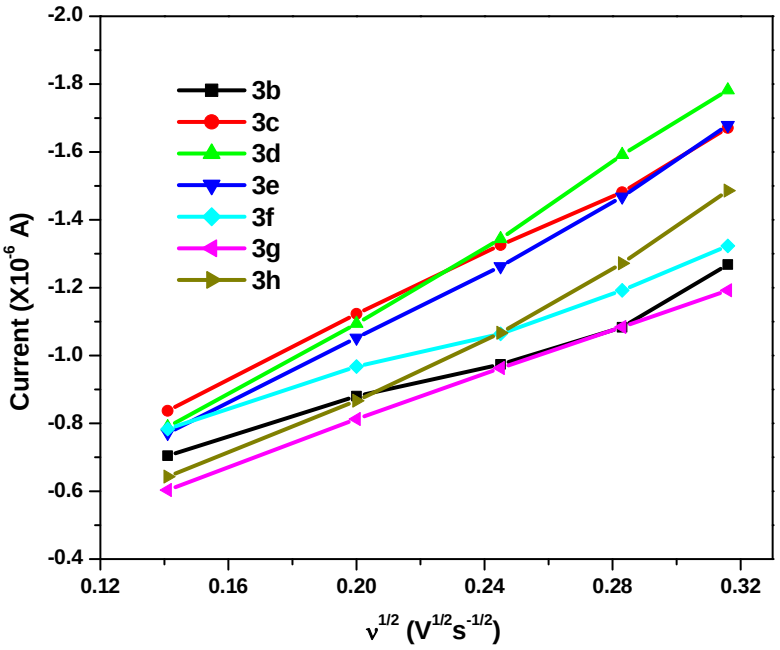


Figure S37: Plot of anodic peak current of ferrocene-carbohydrate conjugates in DMSO solution.

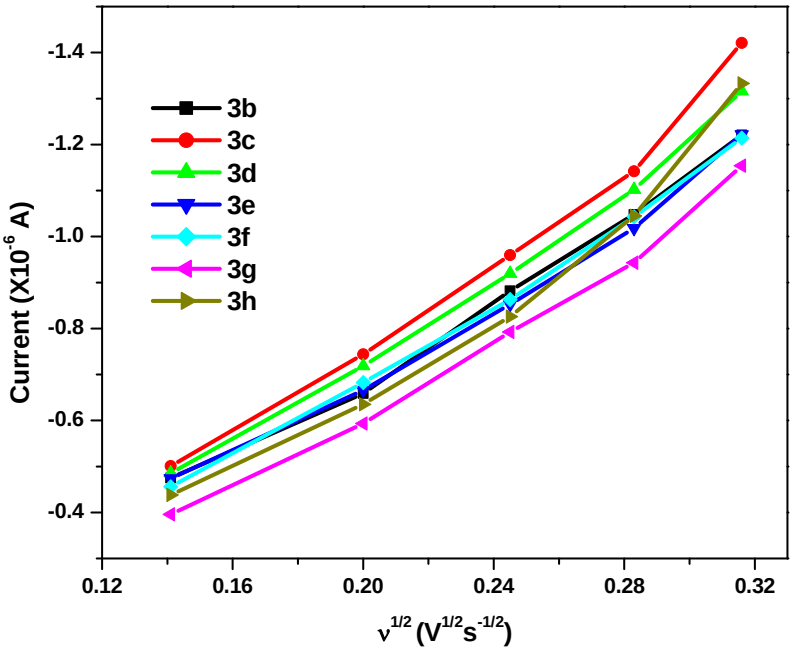


Figure S38: Plot of anodic peak current of ferrocene-carbohydrate conjugates in DMSO-buffer solutions

Table S1: Electrochemical data of ferrocene conjugates

Compound	E_{pa}(mV)	E_{pc}(mV)	ΔE_p(mV)	$E_{1/2}$ *vs* SCE (mV)	i_a/i_c
In DCM					
1	497	370	127	433	0.88
3a	539	366	173	452	0.99
3b	510	391	119	450	0.98
3c	533	370	163	451	1.02
3d	548	364	184	456	1.01
3e	534	364	170	449	0.97
3f	549	372	177	460	1.00
3g	536	354	182	445	0.95
3h	507	368	139	437	0.97
In DMSO					
3b	466	389	77	428	1.00
3c	452	376	76	414	0.99
3d	465	388	77	426	0.98
3e	484	406	78	445	0.98
3f	464	382	82	423	1.00
3g	468	382	86	425	0.99
3h	477	401	76	439	1.02
In DMSO-buffer solution					
3b	390	303	87	347	0.97
3c	387	304	83	346	0.98
3d	387	302	85	344	1.03
3e	385	301	84	343	1.01
3f	385	297	82	341	0.99
3g	395	305	90	350	0.99
3h	393	306	87	349	1.01

Table S2: Crystal data and structure refinement for alkyne **1**.

Empirical formula	$C_{19}H_{16}FeO$	
Formula weight	316.17	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.913(2) Å	α= 90°.
	b = 9.5455(12) Å	β= 99.613(2)°.
	c = 8.8695(11) Å	γ = 90°.
Volume	1495.3(3) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	1.003 mm^{-1}	
F(000)	656	
Crystal size	0.11 x 0.06 x 0.04 mm^3	
θ range for data collection	2.31 to 25.00°.	
Index ranges	-21<=h<=21, -11<=k<=11, -10<=l<=10	
Reflections collected	12814	
Independent reflections	2628 [R(int) = 0.0244]	
Completeness to θ = 25.00°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2628 / 0 / 190	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R1 = 0.0309, wR2 = 0.0808	
R indices (all data)	R1 = 0.0360, wR2 = 0.0842	
Largest diff. peak and hole	0.300 and -0.166 $e.Å^{-3}$	

Table S3: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for alkyne **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-862(2)	5757(4)	-1379(4)	109(1)
C(2)	-537(1)	6136(3)	-2314(3)	80(1)
C(3)	-122(2)	6566(3)	-3510(3)	90(1)
C(4)	1139(1)	5844(3)	-2411(3)	71(1)
C(5)	1239(1)	6918(3)	-1364(3)	68(1)
C(6)	1911(1)	6996(2)	-339(2)	61(1)
C(7)	2483(1)	6031(2)	-328(2)	54(1)
C(8)	2352(2)	4942(2)	-1367(3)	70(1)
C(9)	1689(2)	4854(3)	-2392(3)	79(1)
C(10)	3651(2)	3040(2)	2987(3)	78(1)
C(11)	2922(2)	3582(3)	2916(4)	100(1)
C(12)	2958(3)	4556(4)	4104(6)	126(2)
C(13)	3696(3)	4605(3)	4860(4)	106(1)
C(14)	4113(2)	3677(3)	4183(3)	81(1)
C(15)	3220(1)	6193(2)	673(2)	54(1)
C(16)	3899(1)	5477(3)	523(3)	64(1)
C(17)	4486(1)	5978(3)	1666(3)	72(1)
C(18)	4177(1)	6999(2)	2526(3)	71(1)
C(19)	3399(1)	7127(2)	1928(2)	60(1)
Fe(1)	3646(1)	5127(1)	2633(1)	53(1)
O(1)	522(1)	5703(3)	-3550(2)	98(1)

Table S4: Bond lengths [Å] and angles [°] for alkyne **1**

C(1)-C(2)	1.149(4)
C(1)-H(1)	0.9300
C(2)-C(3)	1.452(4)
C(3)-O(1)	1.423(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(9)	1.365(4)
C(4)-O(1)	1.373(3)
C(4)-C(5)	1.374(3)
C(5)-C(6)	1.384(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.377(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.383(3)
C(7)-C(15)	1.470(3)
C(8)-C(9)	1.371(4)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(14)	1.373(4)
C(10)-C(11)	1.397(4)
C(10)-Fe(1)	2.016(2)
C(10)-H(10)	0.9800
C(11)-C(12)	1.399(5)
C(11)-Fe(1)	2.008(2)
C(11)-H(11)	0.9800
C(12)-C(13)	1.380(6)
C(12)-Fe(1)	2.014(3)
C(12)-H(12)	0.9800
C(13)-C(14)	1.361(4)
C(13)-Fe(1)	2.025(3)
C(13)-H(13)	0.9800
C(14)-Fe(1)	2.030(2)
C(14)-H(14)	0.9800
C(15)-C(19)	1.421(3)
C(15)-C(16)	1.421(3)
C(15)-Fe(1)	2.049(2)

C(16)-C(17)	1.416(3)
C(16)-Fe(1)	2.025(2)
C(16)-H(16)	0.9800
C(17)-C(18)	1.407(3)
C(17)-Fe(1)	2.023(2)
C(17)-H(17)	0.9800
C(18)-C(19)	1.411(3)
C(18)-Fe(1)	2.035(2)
C(18)-H(18)	0.9800
C(19)-Fe(1)	2.0340(19)
C(19)-H(19)	0.9800

C(2)-C(1)-H(1)	180.0
C(1)-C(2)-C(3)	178.1(4)
O(1)-C(3)-C(2)	111.8(2)
O(1)-C(3)-H(3A)	109.3
C(2)-C(3)-H(3A)	109.3
O(1)-C(3)-H(3B)	109.3
C(2)-C(3)-H(3B)	109.3
H(3A)-C(3)-H(3B)	107.9
C(9)-C(4)-O(1)	115.6(2)
C(9)-C(4)-C(5)	119.7(2)
O(1)-C(4)-C(5)	124.7(2)
C(4)-C(5)-C(6)	119.0(2)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(7)-C(6)-C(5)	122.2(2)
C(7)-C(6)-H(6)	118.9
C(5)-C(6)-H(6)	118.9
C(6)-C(7)-C(8)	117.0(2)
C(6)-C(7)-C(15)	121.71(18)
C(8)-C(7)-C(15)	121.14(19)
C(9)-C(8)-C(7)	121.3(2)
C(9)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(4)-C(9)-C(8)	120.6(2)
C(4)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7

C(14)-C(10)-C(11)	108.0(3)
C(14)-C(10)-Fe(1)	70.72(14)
C(11)-C(10)-Fe(1)	69.36(14)
C(14)-C(10)-H(10)	126.0
C(11)-C(10)-H(10)	126.0
Fe(1)-C(10)-H(10)	126.0
C(10)-C(11)-C(12)	106.7(3)
C(10)-C(11)-Fe(1)	70.02(14)
C(12)-C(11)-Fe(1)	69.89(17)
C(10)-C(11)-H(11)	126.6
C(12)-C(11)-H(11)	126.6
Fe(1)-C(11)-H(11)	126.6
C(13)-C(12)-C(11)	108.0(3)
C(13)-C(12)-Fe(1)	70.45(18)
C(11)-C(12)-Fe(1)	69.41(16)
C(13)-C(12)-H(12)	126.0
C(11)-C(12)-H(12)	126.0
Fe(1)-C(12)-H(12)	126.0
C(14)-C(13)-C(12)	108.4(3)
C(14)-C(13)-Fe(1)	70.61(16)
C(12)-C(13)-Fe(1)	69.59(19)
C(14)-C(13)-H(13)	125.8
C(12)-C(13)-H(13)	125.8
Fe(1)-C(13)-H(13)	125.8
C(13)-C(14)-C(10)	109.0(3)
C(13)-C(14)-Fe(1)	70.18(17)
C(10)-C(14)-Fe(1)	69.61(14)
C(13)-C(14)-H(14)	125.5
C(10)-C(14)-H(14)	125.5
Fe(1)-C(14)-H(14)	125.5
C(19)-C(15)-C(16)	106.81(19)
C(19)-C(15)-C(7)	127.02(18)
C(16)-C(15)-C(7)	126.12(18)
C(19)-C(15)-Fe(1)	69.08(11)
C(16)-C(15)-Fe(1)	68.70(12)
C(7)-C(15)-Fe(1)	129.03(13)
C(17)-C(16)-C(15)	108.4(2)
C(17)-C(16)-Fe(1)	69.44(13)

C(15)-C(16)-Fe(1)	70.47(11)
C(17)-C(16)-H(16)	125.8
C(15)-C(16)-H(16)	125.8
Fe(1)-C(16)-H(16)	125.8
C(18)-C(17)-C(16)	108.0(2)
C(18)-C(17)-Fe(1)	70.15(12)
C(16)-C(17)-Fe(1)	69.61(12)
C(18)-C(17)-H(17)	126.0
C(16)-C(17)-H(17)	126.0
Fe(1)-C(17)-H(17)	126.0
C(17)-C(18)-C(19)	108.0(2)
C(17)-C(18)-Fe(1)	69.27(13)
C(19)-C(18)-Fe(1)	69.69(11)
C(17)-C(18)-H(18)	126.0
C(19)-C(18)-H(18)	126.0
Fe(1)-C(18)-H(18)	126.0
C(18)-C(19)-C(15)	108.71(19)
C(18)-C(19)-Fe(1)	69.73(12)
C(15)-C(19)-Fe(1)	70.19(11)
C(18)-C(19)-H(19)	125.6
C(15)-C(19)-H(19)	125.6
Fe(1)-C(19)-H(19)	125.6
C(11)-Fe(1)-C(12)	40.70(15)
C(11)-Fe(1)-C(10)	40.62(11)
C(12)-Fe(1)-C(10)	67.61(12)
C(11)-Fe(1)-C(17)	152.89(14)
C(12)-Fe(1)-C(17)	164.28(19)
C(10)-Fe(1)-C(17)	118.56(11)
C(11)-Fe(1)-C(13)	67.75(15)
C(12)-Fe(1)-C(13)	39.96(16)
C(10)-Fe(1)-C(13)	66.83(12)
C(17)-Fe(1)-C(13)	126.70(16)
C(11)-Fe(1)-C(16)	119.07(13)
C(12)-Fe(1)-C(16)	154.03(19)
C(10)-Fe(1)-C(16)	108.10(10)
C(17)-Fe(1)-C(16)	40.94(9)
C(13)-Fe(1)-C(16)	164.07(15)
C(11)-Fe(1)-C(14)	67.41(11)

C(12)-Fe(1)-C(14)	66.67(14)
C(10)-Fe(1)-C(14)	39.67(10)
C(17)-Fe(1)-C(14)	108.03(11)
C(13)-Fe(1)-C(14)	39.21(12)
C(16)-Fe(1)-C(14)	127.41(11)
C(11)-Fe(1)-C(19)	128.05(11)
C(12)-Fe(1)-C(19)	109.17(11)
C(10)-Fe(1)-C(19)	165.96(10)
C(17)-Fe(1)-C(19)	68.38(10)
C(13)-Fe(1)-C(19)	120.20(11)
C(16)-Fe(1)-C(19)	68.41(9)
C(14)-Fe(1)-C(19)	153.09(10)
C(11)-Fe(1)-C(18)	165.55(13)
C(12)-Fe(1)-C(18)	127.57(16)
C(10)-Fe(1)-C(18)	152.25(11)
C(17)-Fe(1)-C(18)	40.59(10)
C(13)-Fe(1)-C(18)	108.48(13)
C(16)-Fe(1)-C(18)	68.49(10)
C(14)-Fe(1)-C(18)	119.18(11)
C(19)-Fe(1)-C(18)	40.58(9)
C(11)-Fe(1)-C(15)	108.31(10)
C(12)-Fe(1)-C(15)	120.18(15)
C(10)-Fe(1)-C(15)	127.88(10)
C(17)-Fe(1)-C(15)	68.83(9)
C(13)-Fe(1)-C(15)	154.13(13)
C(16)-Fe(1)-C(15)	40.83(8)
C(14)-Fe(1)-C(15)	165.07(10)
C(19)-Fe(1)-C(15)	40.73(8)
C(18)-Fe(1)-C(15)	68.60(9)
C(4)-O(1)-C(3)	118.7(2)

Symmetry transformations used to generate equivalent atoms:

Table S5: Anisotropic displacement parameters ($Å^2 x\ 10^3$)for alkyne **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	85(2)	115(3)	124(3)	23(2)	13(2)	-12(2)
C(2)	65(2)	78(2)	90(2)	9(1)	-6(1)	-3(1)
C(3)	83(2)	105(2)	75(2)	14(2)	-5(1)	8(2)
C(4)	68(1)	83(2)	60(1)	-3(1)	11(1)	-1(1)
C(5)	64(1)	67(1)	74(1)	2(1)	20(1)	8(1)
C(6)	65(1)	54(1)	67(1)	-6(1)	23(1)	-4(1)
C(7)	63(1)	48(1)	55(1)	1(1)	22(1)	-4(1)
C(8)	73(2)	59(1)	78(2)	-14(1)	14(1)	7(1)
C(9)	86(2)	74(2)	74(2)	-22(1)	8(1)	1(1)
C(10)	107(2)	40(1)	91(2)	7(1)	31(2)	6(1)
C(11)	69(2)	81(2)	143(3)	55(2)	1(2)	-24(2)
C(12)	151(3)	80(2)	180(4)	65(3)	125(3)	49(2)
C(13)	189(4)	68(2)	72(2)	9(1)	52(2)	5(2)
C(14)	84(2)	71(2)	86(2)	23(1)	8(1)	4(1)
C(15)	61(1)	47(1)	58(1)	2(1)	22(1)	-5(1)
C(16)	63(1)	70(1)	65(1)	-1(1)	30(1)	-6(1)
C(17)	59(1)	79(2)	82(2)	8(1)	21(1)	-13(1)
C(18)	81(2)	56(1)	74(2)	4(1)	8(1)	-20(1)
C(19)	78(1)	40(1)	62(1)	3(1)	15(1)	-4(1)
Fe(1)	59(1)	43(1)	62(1)	2(1)	21(1)	1(1)
O(1)	81(1)	133(2)	76(1)	-19(1)	-3(1)	12(1)

Table S6: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for alkyne **1**.

	x	y	z	U(eq)
H(1)	-1126	5451	-622	130
H(3A)	-454	6519	-4491	108
H(3B)	41	7530	-3337	108
H(5)	861	7582	-1344	81
H(6)	1979	7726	365	73
H(8)	2720	4256	-1371	84
H(9)	1615	4112	-3080	94
H(10)	3805	2324	2309	93
H(11)	2469	3307	2197	120
H(12)	2533	5103	4359	151
H(13)	3887	5202	5739	127
H(14)	4656	3503	4489	97
H(16)	3952	4757	-239	77
H(17)	5015	5669	1827	86
H(18)	4452	7522	3396	85
H(19)	3041	7751	2319	72

Table S7: Torsion angles [°] for alkyne **1**.

C(1)-C(2)-C(3)-O(1)	-42(9)
C(9)-C(4)-C(5)-C(6)	2.1(4)
O(1)-C(4)-C(5)-C(6)	-175.4(2)
C(4)-C(5)-C(6)-C(7)	-0.3(3)
C(5)-C(6)-C(7)-C(8)	-1.7(3)
C(5)-C(6)-C(7)-C(15)	174.51(19)
C(6)-C(7)-C(8)-C(9)	1.8(4)
C(15)-C(7)-C(8)-C(9)	-174.4(2)
O(1)-C(4)-C(9)-C(8)	175.8(2)
C(5)-C(4)-C(9)-C(8)	-1.9(4)
C(7)-C(8)-C(9)-C(4)	-0.1(4)
C(14)-C(10)-C(11)-C(12)	-0.2(3)
Fe(1)-C(10)-C(11)-C(12)	-60.61(18)
C(14)-C(10)-C(11)-Fe(1)	60.44(17)
C(10)-C(11)-C(12)-C(13)	0.5(3)
Fe(1)-C(11)-C(12)-C(13)	-60.2(2)
C(10)-C(11)-C(12)-Fe(1)	60.69(18)
C(11)-C(12)-C(13)-C(14)	-0.7(3)
Fe(1)-C(12)-C(13)-C(14)	-60.2(2)
C(11)-C(12)-C(13)-Fe(1)	59.5(2)
C(12)-C(13)-C(14)-C(10)	0.6(3)
Fe(1)-C(13)-C(14)-C(10)	-58.96(19)
C(12)-C(13)-C(14)-Fe(1)	59.6(2)
C(11)-C(10)-C(14)-C(13)	-0.3(3)
Fe(1)-C(10)-C(14)-C(13)	59.31(19)
C(11)-C(10)-C(14)-Fe(1)	-59.59(17)
C(6)-C(7)-C(15)-C(19)	13.7(3)
C(8)-C(7)-C(15)-C(19)	-170.3(2)
C(6)-C(7)-C(15)-C(16)	-163.6(2)
C(8)-C(7)-C(15)-C(16)	12.5(3)
C(6)-C(7)-C(15)-Fe(1)	105.7(2)
C(8)-C(7)-C(15)-Fe(1)	-78.3(3)
C(19)-C(15)-C(16)-C(17)	-0.5(2)
C(7)-C(15)-C(16)-C(17)	177.20(18)
Fe(1)-C(15)-C(16)-C(17)	-59.28(15)
C(19)-C(15)-C(16)-Fe(1)	58.79(13)

C(7)-C(15)-C(16)-Fe(1)	-123.52(19)
C(15)-C(16)-C(17)-C(18)	0.1(3)
Fe(1)-C(16)-C(17)-C(18)	-59.86(16)
C(15)-C(16)-C(17)-Fe(1)	59.91(15)
C(16)-C(17)-C(18)-C(19)	0.4(3)
Fe(1)-C(17)-C(18)-C(19)	-59.12(15)
C(16)-C(17)-C(18)-Fe(1)	59.53(16)
C(17)-C(18)-C(19)-C(15)	-0.7(2)
Fe(1)-C(18)-C(19)-C(15)	-59.57(13)
C(17)-C(18)-C(19)-Fe(1)	58.86(15)
C(16)-C(15)-C(19)-C(18)	0.7(2)
C(7)-C(15)-C(19)-C(18)	-176.92(18)
Fe(1)-C(15)-C(19)-C(18)	59.29(14)
C(16)-C(15)-C(19)-Fe(1)	-58.55(14)
C(7)-C(15)-C(19)-Fe(1)	123.79(19)
C(10)-C(11)-Fe(1)-C(12)	-117.3(3)
C(12)-C(11)-Fe(1)-C(10)	117.3(3)
C(10)-C(11)-Fe(1)-C(17)	48.3(3)
C(12)-C(11)-Fe(1)-C(17)	165.6(3)
C(10)-C(11)-Fe(1)-C(13)	-79.9(2)
C(12)-C(11)-Fe(1)-C(13)	37.4(2)
C(10)-C(11)-Fe(1)-C(16)	84.14(19)
C(12)-C(11)-Fe(1)-C(16)	-158.6(2)
C(10)-C(11)-Fe(1)-C(14)	-37.30(17)
C(12)-C(11)-Fe(1)-C(14)	80.0(2)
C(10)-C(11)-Fe(1)-C(19)	168.43(14)
C(12)-C(11)-Fe(1)-C(19)	-74.3(2)
C(10)-C(11)-Fe(1)-C(18)	-157.4(4)
C(12)-C(11)-Fe(1)-C(18)	-40.2(5)
C(10)-C(11)-Fe(1)-C(15)	127.43(17)
C(12)-C(11)-Fe(1)-C(15)	-115.3(2)
C(13)-C(12)-Fe(1)-C(11)	118.9(3)
C(13)-C(12)-Fe(1)-C(10)	80.2(2)
C(11)-C(12)-Fe(1)-C(10)	-38.75(18)
C(13)-C(12)-Fe(1)-C(17)	-36.3(5)
C(11)-C(12)-Fe(1)-C(17)	-155.2(4)
C(11)-C(12)-Fe(1)-C(13)	-118.9(3)
C(13)-C(12)-Fe(1)-C(16)	165.7(2)

C(11)-C(12)-Fe(1)-C(16)	46.8(3)
C(13)-C(12)-Fe(1)-C(14)	36.96(18)
C(11)-C(12)-Fe(1)-C(14)	-81.95(19)
C(13)-C(12)-Fe(1)-C(19)	-114.47(19)
C(11)-C(12)-Fe(1)-C(19)	126.62(18)
C(13)-C(12)-Fe(1)-C(18)	-72.8(2)
C(11)-C(12)-Fe(1)-C(18)	168.29(16)
C(13)-C(12)-Fe(1)-C(15)	-157.92(17)
C(11)-C(12)-Fe(1)-C(15)	83.17(19)
C(14)-C(10)-Fe(1)-C(11)	-118.8(3)
C(14)-C(10)-Fe(1)-C(12)	-80.0(2)
C(11)-C(10)-Fe(1)-C(12)	38.8(2)
C(14)-C(10)-Fe(1)-C(17)	84.01(18)
C(11)-C(10)-Fe(1)-C(17)	-157.21(19)
C(14)-C(10)-Fe(1)-C(13)	-36.5(2)
C(11)-C(10)-Fe(1)-C(13)	82.3(2)
C(14)-C(10)-Fe(1)-C(16)	127.38(17)
C(11)-C(10)-Fe(1)-C(16)	-113.8(2)
C(11)-C(10)-Fe(1)-C(14)	118.8(3)
C(14)-C(10)-Fe(1)-C(19)	-159.4(3)
C(11)-C(10)-Fe(1)-C(19)	-40.6(5)
C(14)-C(10)-Fe(1)-C(18)	49.3(3)
C(11)-C(10)-Fe(1)-C(18)	168.1(2)
C(14)-C(10)-Fe(1)-C(15)	168.42(15)
C(11)-C(10)-Fe(1)-C(15)	-72.8(2)
C(18)-C(17)-Fe(1)-C(11)	170.4(2)
C(16)-C(17)-Fe(1)-C(11)	51.4(3)
C(18)-C(17)-Fe(1)-C(12)	-46.5(5)
C(16)-C(17)-Fe(1)-C(12)	-165.5(4)
C(18)-C(17)-Fe(1)-C(10)	-155.98(15)
C(16)-C(17)-Fe(1)-C(10)	84.97(17)
C(18)-C(17)-Fe(1)-C(13)	-74.8(2)
C(16)-C(17)-Fe(1)-C(13)	166.18(15)
C(18)-C(17)-Fe(1)-C(16)	119.0(2)
C(18)-C(17)-Fe(1)-C(14)	-114.10(16)
C(16)-C(17)-Fe(1)-C(14)	126.86(16)
C(18)-C(17)-Fe(1)-C(19)	37.52(14)
C(16)-C(17)-Fe(1)-C(19)	-81.53(15)

C(16)-C(17)-Fe(1)-C(18)	-119.0(2)
C(18)-C(17)-Fe(1)-C(15)	81.41(15)
C(16)-C(17)-Fe(1)-C(15)	-37.64(14)
C(14)-C(13)-Fe(1)-C(11)	81.1(2)
C(12)-C(13)-Fe(1)-C(11)	-38.08(19)
C(14)-C(13)-Fe(1)-C(12)	119.2(3)
C(14)-C(13)-Fe(1)-C(10)	36.88(18)
C(12)-C(13)-Fe(1)-C(10)	-82.3(2)
C(14)-C(13)-Fe(1)-C(17)	-72.4(2)
C(12)-C(13)-Fe(1)-C(17)	168.5(2)
C(14)-C(13)-Fe(1)-C(16)	-37.6(5)
C(12)-C(13)-Fe(1)-C(16)	-156.7(4)
C(12)-C(13)-Fe(1)-C(14)	-119.2(3)
C(14)-C(13)-Fe(1)-C(19)	-156.75(17)
C(12)-C(13)-Fe(1)-C(19)	84.1(2)
C(14)-C(13)-Fe(1)-C(18)	-113.8(2)
C(12)-C(13)-Fe(1)-C(18)	127.0(2)
C(14)-C(13)-Fe(1)-C(15)	167.30(19)
C(12)-C(13)-Fe(1)-C(15)	48.1(4)
C(17)-C(16)-Fe(1)-C(11)	-155.96(16)
C(15)-C(16)-Fe(1)-C(11)	84.62(16)
C(17)-C(16)-Fe(1)-C(12)	171.1(2)
C(15)-C(16)-Fe(1)-C(12)	51.7(3)
C(17)-C(16)-Fe(1)-C(10)	-113.00(16)
C(15)-C(16)-Fe(1)-C(10)	127.57(14)
C(15)-C(16)-Fe(1)-C(17)	-119.4(2)
C(17)-C(16)-Fe(1)-C(13)	-44.3(5)
C(15)-C(16)-Fe(1)-C(13)	-163.7(4)
C(17)-C(16)-Fe(1)-C(14)	-73.31(19)
C(15)-C(16)-Fe(1)-C(14)	167.26(13)
C(17)-C(16)-Fe(1)-C(19)	81.47(15)
C(15)-C(16)-Fe(1)-C(19)	-37.96(12)
C(17)-C(16)-Fe(1)-C(18)	37.69(15)
C(15)-C(16)-Fe(1)-C(18)	-81.74(14)
C(17)-C(16)-Fe(1)-C(15)	119.4(2)
C(13)-C(14)-Fe(1)-C(11)	-82.0(2)
C(10)-C(14)-Fe(1)-C(11)	38.18(18)
C(13)-C(14)-Fe(1)-C(12)	-37.6(2)

C(10)-C(14)-Fe(1)-C(12)	82.6(2)
C(13)-C(14)-Fe(1)-C(10)	-120.2(3)
C(13)-C(14)-Fe(1)-C(17)	126.5(2)
C(10)-C(14)-Fe(1)-C(17)	-113.28(17)
C(10)-C(14)-Fe(1)-C(13)	120.2(3)
C(13)-C(14)-Fe(1)-C(16)	167.8(2)
C(10)-C(14)-Fe(1)-C(16)	-71.97(19)
C(13)-C(14)-Fe(1)-C(19)	48.9(3)
C(10)-C(14)-Fe(1)-C(19)	169.13(19)
C(13)-C(14)-Fe(1)-C(18)	83.7(2)
C(10)-C(14)-Fe(1)-C(18)	-156.14(15)
C(13)-C(14)-Fe(1)-C(15)	-158.1(4)
C(10)-C(14)-Fe(1)-C(15)	-37.9(4)
C(18)-C(19)-Fe(1)-C(11)	167.56(18)
C(15)-C(19)-Fe(1)-C(11)	-72.67(19)
C(18)-C(19)-Fe(1)-C(12)	125.9(2)
C(15)-C(19)-Fe(1)-C(12)	-114.3(2)
C(18)-C(19)-Fe(1)-C(10)	-159.9(4)
C(15)-C(19)-Fe(1)-C(10)	-40.1(4)
C(18)-C(19)-Fe(1)-C(17)	-37.52(14)
C(15)-C(19)-Fe(1)-C(17)	82.24(14)
C(18)-C(19)-Fe(1)-C(13)	83.3(2)
C(15)-C(19)-Fe(1)-C(13)	-156.89(19)
C(18)-C(19)-Fe(1)-C(16)	-81.72(14)
C(15)-C(19)-Fe(1)-C(16)	38.05(12)
C(18)-C(19)-Fe(1)-C(14)	49.9(3)
C(15)-C(19)-Fe(1)-C(14)	169.6(2)
C(15)-C(19)-Fe(1)-C(18)	119.76(18)
C(18)-C(19)-Fe(1)-C(15)	-119.76(18)
C(17)-C(18)-Fe(1)-C(11)	-162.3(4)
C(19)-C(18)-Fe(1)-C(11)	-42.8(5)
C(17)-C(18)-Fe(1)-C(12)	165.6(2)
C(19)-C(18)-Fe(1)-C(12)	-74.9(2)
C(17)-C(18)-Fe(1)-C(10)	50.2(3)
C(19)-C(18)-Fe(1)-C(10)	169.67(19)
C(19)-C(18)-Fe(1)-C(17)	119.5(2)
C(17)-C(18)-Fe(1)-C(13)	125.34(19)
C(19)-C(18)-Fe(1)-C(13)	-115.16(18)

C(17)-C(18)-Fe(1)-C(16)	-38.01(14)
C(19)-C(18)-Fe(1)-C(16)	81.49(14)
C(17)-C(18)-Fe(1)-C(14)	83.85(17)
C(19)-C(18)-Fe(1)-C(14)	-156.65(14)
C(17)-C(18)-Fe(1)-C(19)	-119.5(2)
C(17)-C(18)-Fe(1)-C(15)	-82.03(15)
C(19)-C(18)-Fe(1)-C(15)	37.47(12)
C(19)-C(15)-Fe(1)-C(11)	127.65(16)
C(16)-C(15)-Fe(1)-C(11)	-113.57(17)
C(7)-C(15)-Fe(1)-C(11)	6.3(2)
C(19)-C(15)-Fe(1)-C(12)	84.6(2)
C(16)-C(15)-Fe(1)-C(12)	-156.6(2)
C(7)-C(15)-Fe(1)-C(12)	-36.7(3)
C(19)-C(15)-Fe(1)-C(10)	168.58(14)
C(16)-C(15)-Fe(1)-C(10)	-72.64(16)
C(7)-C(15)-Fe(1)-C(10)	47.2(2)
C(19)-C(15)-Fe(1)-C(17)	-81.04(14)
C(16)-C(15)-Fe(1)-C(17)	37.74(14)
C(7)-C(15)-Fe(1)-C(17)	157.6(2)
C(19)-C(15)-Fe(1)-C(13)	51.1(3)
C(16)-C(15)-Fe(1)-C(13)	169.8(3)
C(7)-C(15)-Fe(1)-C(13)	-70.3(4)
C(19)-C(15)-Fe(1)-C(16)	-118.78(18)
C(7)-C(15)-Fe(1)-C(16)	119.9(2)
C(19)-C(15)-Fe(1)-C(14)	-161.6(3)
C(16)-C(15)-Fe(1)-C(14)	-42.8(4)
C(7)-C(15)-Fe(1)-C(14)	77.1(4)
C(16)-C(15)-Fe(1)-C(19)	118.78(18)
C(7)-C(15)-Fe(1)-C(19)	-121.3(2)
C(19)-C(15)-Fe(1)-C(18)	-37.34(12)
C(16)-C(15)-Fe(1)-C(18)	81.44(14)
C(7)-C(15)-Fe(1)-C(18)	-158.7(2)
C(9)-C(4)-O(1)-C(3)	170.8(3)
C(5)-C(4)-O(1)-C(3)	-11.6(4)
C(2)-C(3)-O(1)-C(4)	-72.8(3)

Symmetry transformations used to generate equivalent atoms: